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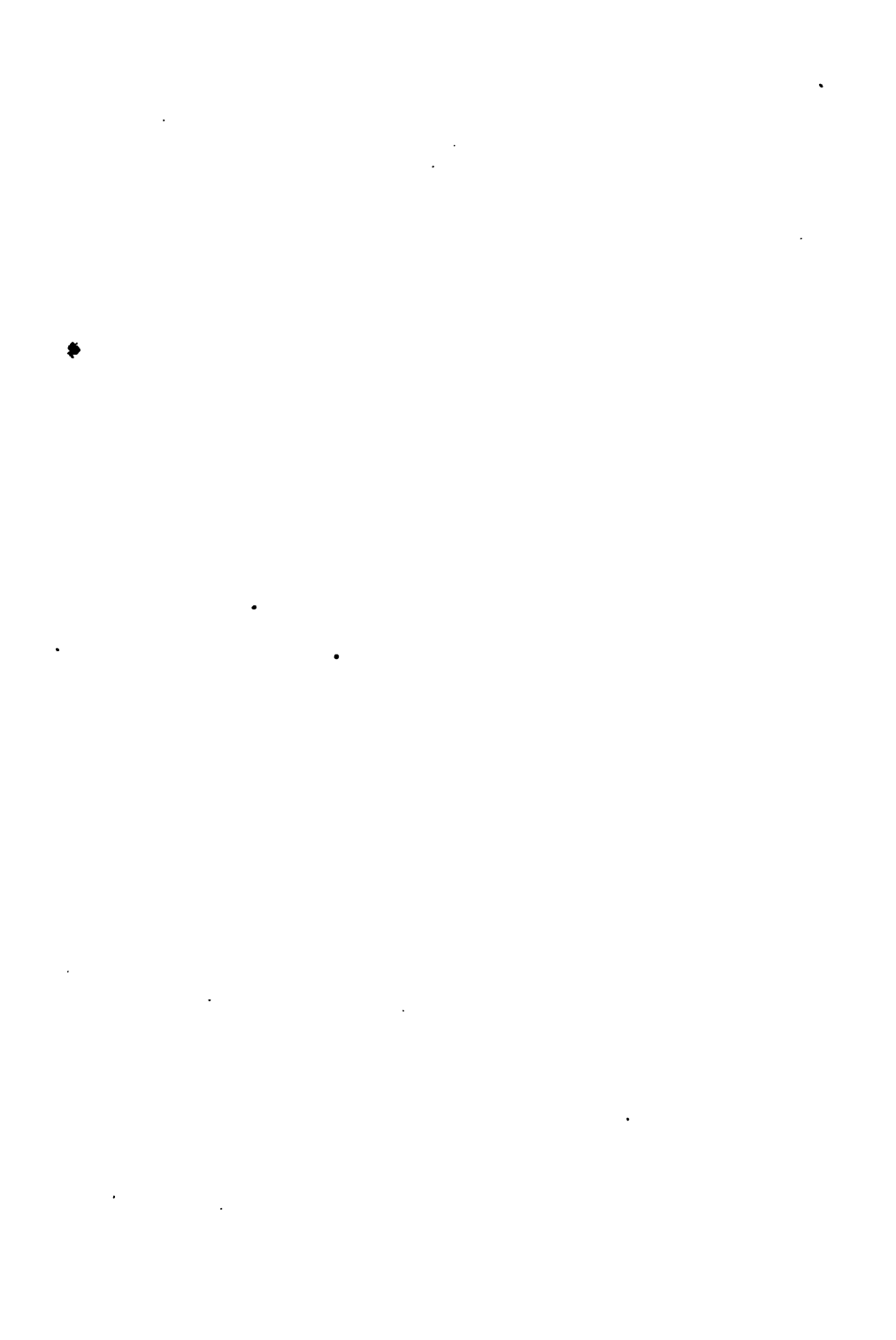
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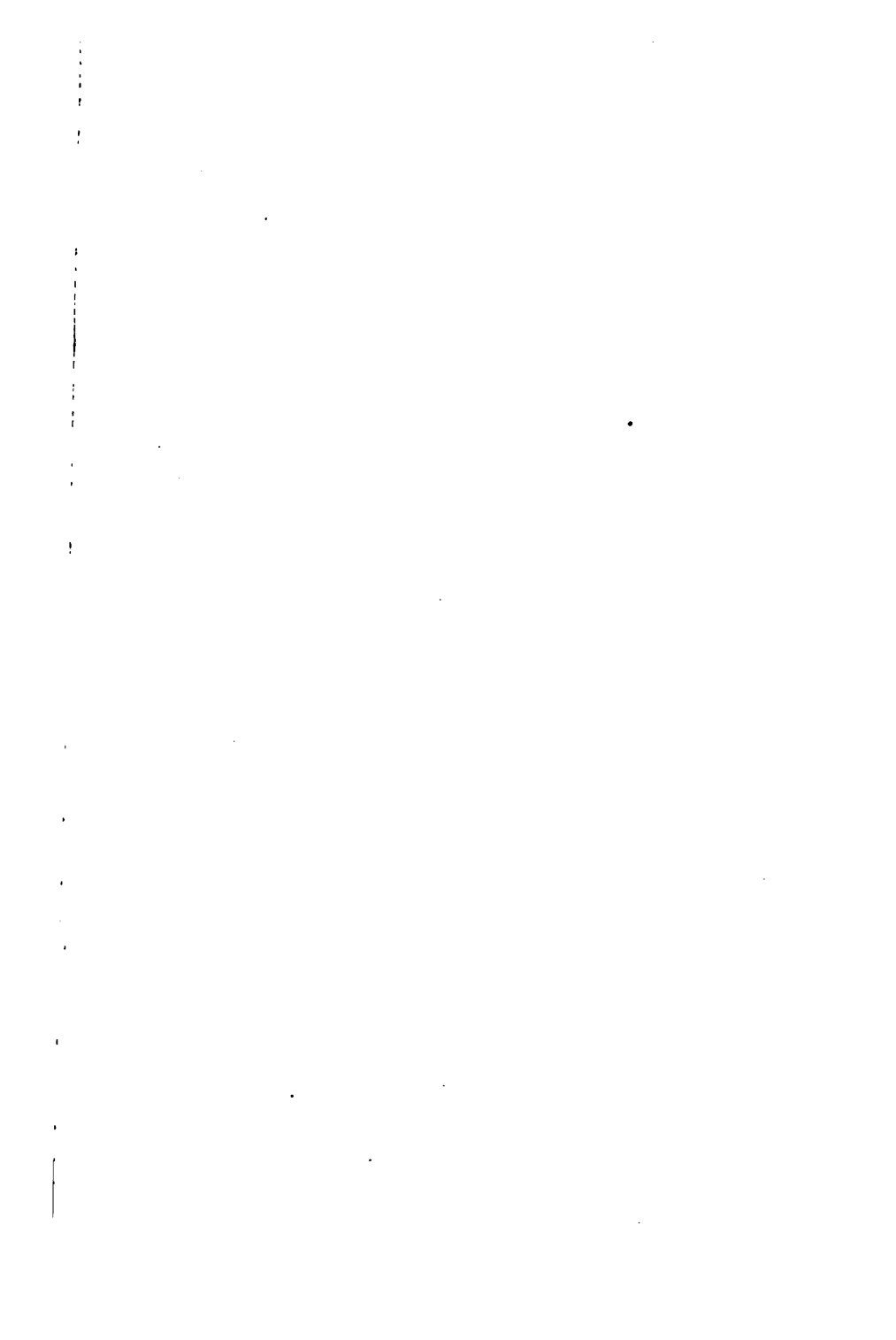
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AN ELEMENTARY

MANUAL OF CHEMISTRY

BY

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*BEING A REVISION AND REWRITING OF PROFESSOR
W. R. NICHOLS'S ABRIDGMENT OF ELIOT
AND STORER'S MANUAL*



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PREFACE.

THIS book is the lineal descendant of the "Manual of Inorganic Chemistry" of Eliot and Storer, and the "Elementary Manual of Chemistry" of Eliot, Storer, and Nichols. It is, in fact, the last-named book thoroughly revised and rewritten, and somewhat enlarged, in order that it may meet the requirements of the present day and represent more nearly the present condition of chemical knowledge.

The purpose of the book, like that of its predecessors, is to facilitate the teaching of chemistry by the experimental and inductive method. By means of it the careful student may acquaint himself with the main facts and principles of the science, through the attentive use of his own perceptive faculties, by a process not unlike that by which these facts and principles were first established. The authors believe that the study of a science of observation ought to develop and discipline the observing faculties, and that such a study fails of its true end if it become either a mere exercise of the memory or little more than a training in speculative methods of thought.

The minute instructions given in the descriptions of experiments, and printed in the smaller type, are intended to enable the student to see, smell, and touch for himself. These detailed descriptions are meant for laboratory use. Pains have been taken to simplify the experiments to the utmost, and to choose such as have been found to stand the

test of actual performance by students; and, in order to mark as clearly as possible the distinction between chemistry and chemical manipulation, the necessary instructions on the latter subject have been put in an appendix. In cases in which it is impossible for every student to experiment for himself, the authors hope that this manual will make it easy for the teacher, even if he be not a professional chemist, to exhibit to his class, in a familiar and inexpensive manner, experiments enough to supply ocular demonstration of the leading facts and generalizations of the science.

This book is not written in the interest of any particular theory, or of any one system of nomenclature or of notation. The intention is to exhibit, so far as possible within the limits proper to an elementary manual, the present state of chemical science, and the relations of the science to its practical applications.

APRIL, 1894.

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ELEMENTARY

MANUAL OF CHEMISTRY.



INTRODUCTION.

1. THE various objects which constitute external nature present to the observing eye an infinite variety of quality and circumstance. Some bodies are hard, others soft; some are brittle, others tough or elastic. Some natural objects are endowed with life,—they grow; others are lifeless,—they may be moved, but do not move themselves. Some bodies are in a state of incessant change; while others are so immovable and unchangeable that they seem everlasting. In the midst of this infinite diversity of external objects, where lies the domain of *Chemistry*? What is the subject-matter of this science?

When air moves in wind, when water moves in tides or in the fall of rain or snow, the air and water remain air and water still: their constitution is not changed by the motion, however frequent or however great. A bit of granite, thrown off from the ledge by frost, is still a bit of granite, and no new or altered thing. If a solid piece of iron be reduced to filings, each finest morsel is metallic iron still, of the same substance as the original piece, as will appear to the eye if a morsel be sufficiently magnified under the microscope. The melted, fluid lead in the hot crucible, and the solid lead of the cold bullet cast from it, are the same in substance, differing only in respect to temperature. In all these cases, the changes are external and nonessential, not intimate and constitutional: they do not

affect the composition of substances. They are called *physical* changes.

2. When iron is exposed to the weather, it becomes covered with a brownish, earthy coating, which bears no outward resemblance to the original iron; and, if exposed long enough, the metal completely disappears, being wholly changed into this very different substance, *rust*. A piece of coal burns in the grate, and soon vanishes, leaving nothing but a little ashes. Dead vegetable or animal matters, when left exposed to moist air, soon putrefy, decay, and disappear. So, too, the fragment of granite which frost has broken from the ledge, exposed for centuries to the action of the air and rain, becomes changed: it "weathers," and after a time could no longer be recognized as granite. All these changes involve alterations in the intimate constitution of the bodies which undergo them: the substances lose their original properties, and bodies having new and different properties are formed. Such changes as these are called *chemical* changes.

Experiment 1.— Mix thoroughly 3 grams (for Tables of the Metric System of Weights and Measures, see Appendix) of coarsely powdered sulphur with 8 g. of copper filings or fine turnings. Put the mixture into a tube of hard glass (No. 3) about 12 cm. long, and closed at one end (Appendix, §§ 1-4). Hold the tube by the open end with the wooden nippers, as in Fig. 1, and heat the mixture over the gas lamp (Appendix, § 5), until it suddenly glows vividly at the instant when the copper and sulphur combine. When no further change takes place, allow the tube to cool; break it and examine the contents.

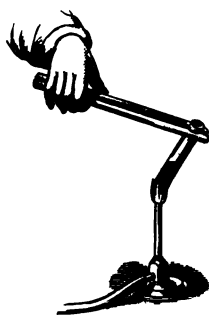


Fig. 1.

Before heat was applied, the mixture of the two substances was simply mechanical, and the copper might have been completely separated from the sulphur by due care and patience; but, during the ignition, the copper and sulphur have united chemically, and there has been formed a substance, which, while containing both, has no external resemblance to either. It is a chemical compound. In the new body the eye can detect neither copper nor sulphur; and the two bodies cannot be separated by any purely mechanical means, such as sifting, washing, using a magnet, etc.

Processes by which the whole character and appearance of the bodies concerned are changed, as in this experiment, so that essentially new bodies are formed from the old, are *chemical* processes. It is the function of the chemist, on the one hand, to investigate the action of each substance on every other, and to study the properties of the combinations resulting from this action; and, on the other, to separate compound bodies into their simpler constituents: he further seeks the general laws by which the intimate combinations of matter are controlled. With these ends in view, he endeavors to pull to pieces, or, in technical language, to *analyze*, every natural substance on which he lays hands. Having thus found out the composition of the substance, he seeks to put it together again, or to recompose it out of its constituent parts. By one or both of these two processes, — *analysis* (unloosing) and *synthesis* (putting together), — the chemist studies all substances.

3. The first question which the chemist asks himself concerning every natural substance is, *Of what is it composed?* He then attempts to resolve the substance into simpler constituents. If he succeeds in decomposing it, he obtains the answer to this first question; if the body cannot be decomposed by any known method of analysis, the substance must be regarded as being already at its simplest. Such simple bodies are called *elements*. Secondly, the chemist asks, *How does this new substance comport itself when brought into contact with other substances already familiar?* About seventy substances are at present admitted to be simple, primary substances, or elements. Other elementary substances may hereafter be discovered, and substances which are now regarded as elements may hereafter be found to be compound; so that the number of the substances considered as elements is subject to change. Of compound bodies, formed by the union of these elements with each other, we find a series, numbering many thousands, in the inorganic kingdom of nature, comprising all the diversified mineral constituents of the earth's crust; while another series, far more complex in composition, and almost innumerable in multitude, exists in the vegetable and animal world. The task of the chemist in thoroughly answering his second question would

clearly be endless, were it not for the existence of general properties common to extensive groups of both elementary and compound bodies, and of general laws which chemical processes invariably obey.

While, therefore, the chemist seeks the answers to the two fundamental questions above stated, he is at the same time inquiring what relations exist between the properties of a body and its composition; and he is also studying that natural and invariable sequence of chemical phenomena, which, when fully known, will constitute the perfect science of chemistry.

4. Generalizations from observed facts, so long as they are uncertain and incomplete, are called *hypotheses* and *theories*; when tolerably complete and reasonably certain, they are called *laws*. The attention of the student should be constantly directed to the keen discrimination between facts and the speculations founded upon those facts; between the actual evidence of our trained senses brought intelligently to bear upon chemical phenomena, and the reasonings and abstract conclusions based upon this evidence; between, in short, that which we may know and that which we may believe.

CHAPTER I.

AIR.

5. We are everywhere surrounded by an atmosphere of invisible gas, called *air*. In motion, it is wind, and we recognize its existence by its powerful effects; but in the stillest places it exists as well. The presence of air in any bottle, flask, or other hollow vessel which is empty, in the sense in which this word is ordinarily applied, can be shown very simply by attempting to put some other substance into the vessel, under such conditions that the air cannot pass out from it.

If, for example, we wrap around the throat of a funnel with narrow outlet a strip of moistened cloth or paper, so that the funnel shall fit tightly into the neck of a bottle, and then fill the funnel with water,

we shall observe that this water does not run into the bottle. The bottle which we have called empty is in reality filled with air, and it is this air which prevents the water from entering the bottle. If, now, the funnel be lifted slightly, so that the mouth of the bottle shall no longer be completely closed by it, the air within the bottle will pass out, and the water in the funnel will instantly flow down.

6. We may actually pump the air out of the bottle by means of an apparatus known as the air pump, or we may remove a portion of the air by suction.

Exp. 2. — Fit to any small flask or bottle a perforated cork (Appendix, § 9), to which has been adapted a short piece of glass tubing (No. 7). Slip over the end of this glass tube a short piece of caoutchouc tubing. Suck part of the air out of the flask, and then nip the caoutchouc tube with thumb and finger, so that no air shall reënter. Immerse the neck of the flask in a basin of water, and release the caoutchouc tube. Water will instantly rise into the flask to take the place of the air which has been sucked out.

7. The water, in this experiment, is forced into the flask by the pressure of the superincumbent atmosphere. Air has weight; that is to say, it is subject to the law of gravitation. It has been determined that the force with which the air is attracted to the earth is, on an average, equal to a weight of 1.033 kilo to the square centimeter of surface; hence the ocean of air above us presses down upon every square centimeter of the earth's surface with a force equal to that which would be exerted by a bar of metal, or other substance, a centimeter square in section, and long enough to weigh 1.033 kilo. If such a bar were constructed of iron, it would be 1.3 m. long; if of water, — and a bar of this substance can readily be made by inclosing the water in a tube, — it would be 10.33 m. long; if of mercury, 760 mm. long. A liter of dry air at the temperature of 0° Centigrade¹ (Appendix, § 30) and under a pressure of 760 mm. of mercury, that is to say under a pressure which will support a column of mercury 760 mm. high, weighs 1.2932 g.

In addition to the qualities already mentioned, we find air

¹ The Centigrade thermometer is used throughout this work.

to be tasteless and odorless ; it is also colorless when in small depths, but exhibits a blue tint when seen in large masses, as when in the absence of clouds we look at the sky or at a distant mountain.

8. We will now proceed to study the **chemical properties** of air, first asking the question, *Of what is air composed?* When a bar of iron is heated in the air, as at a blacksmith's forge, it becomes covered with a coating, which flies off in scales when the iron is beaten upon the anvil. If a piece of wire or ribbon made of the metal magnesium be touched with a match, it will take fire and burn, and be entirely converted into white ashes. With the exception of gold, silver, platinum, and a few other exceedingly rare metals, all the metals burn, or rust, when heated in the air. If no air be present, this rust or ashes will not be formed, however long or intensely the metal may be heated. But in what manner is the rust formed? Is something driven out of the metal into the air, or does something come out of the air and unite with the metal? This question may be answered by experiment. If a weighed quantity of tin foil be heated in a porcelain dish over the gas lamp, the metal is gradually converted into white ashes. When all the metal has thus been changed, and the ashes have been allowed to cool, it will be found that the ashes are very sensibly heavier than the original metal.

9. It is possible that during the heating the metal may have lost something, but it is certain that it has gained more. We have therefore taken something out of the air, which, gaseous in the air, has become solid in the white ashes of the tin. It would be possible to recover from the tin rust the something thus taken from the atmosphere, and to compare it with common air, and so learn whether the matter which combined with the heated tin is air itself, or only a part of the air; but the process would be a circuitous one. From the rust of some metals, however, as from that of mercury, the absorbed gas can be very easily expelled. Mercury rust may be prepared by heating the metal for a long time in the air, but there are other easier methods of obtaining the substance known as *red oxide of mercury*.

Exp. 3. — Put into a tube of hard glass (No. 2) about 12 cm. long 10 g. of the red oxide of mercury (mercuric oxide). Tubes of hard glass, for such purposes, will be hereafter designated as *ignition tubes*. Attach to this ignition tube, by means of a perforated cork or caoutchouc stopper, a delivery tube of glass (No. 8), of such shape and length that it shall reach beneath the inverted saucer in the pan of water, as represented in Fig. 2. The lower end of the ignition tube should be about 4 cm. above the top of the lamp. The tube may be supported on the iron stand, and should be inclined as represented in the figure. (See also Appendix, § 11.)

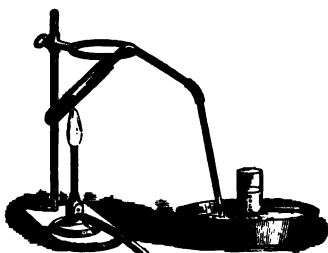


Fig. 2.

Upon heating the ignition tube, gas will begin to escape from the delivery tube, and bubble up through the water. The first portion is simply the atmospheric air which filled the tubes at the beginning of the experiment, and which is expanded by heat. This air may be collected in a small bottle by itself, and thrown away. The volume of gas thus thrown away should not be much greater than that of the tubes. As the ignition tube becomes hotter, gas will be freely given off from the mercuric oxide contained in it, and should be collected in bottles of 100 to 150 cc. capacity.

It is necessary to avoid heating intensely any single small spot of the ignition tube, lest the glass soften, and, yielding to the pressure from within, blow outward, and so spoil the tube and arrest the experiment. The gas flame should be so placed and regulated as to heat 3 or 4 cm. of the tube at once.

As soon as the disengagement of gas slackens, lift the iron stand up, and take the delivery tube out of the water, taking care that no water remains in the end of the tube. Then, *and not till then*, extinguish the lamp (Appendix, § 11). In the upper part of the ignition tube, and sometimes in the delivery tube also, metallic mercury will be found condensed in minute globules. The liquid metal is volatile at the temperature to which it has been subjected, and has distilled away from the hot part of the tube, and condensed upon the cooler part.

Slip a glass plate under the mouth of the bottle, and, while holding it there, turn the bottle so that it shall stand upright. Remove the plate and thrust a lighted splinter of soft wood into the gas: it will burn with much greater brilliancy than in the air. A glowing match put into the gas will burn freely. So, too, if a candle which has just

been extinguished be placed, while the wick still glows, in another bottle of the gas, the glowing wick will burst into flame, and the candle will burn with extraordinary brightness.

10. It is very obvious, from these experiments, that the gas which enters into the composition of mercury rust is not air itself; but since it came originally from the air, if it is not the whole of air, it must be a part of air. It has indeed been found to be a constant constituent of the air, and a chemical element of very various powers and great importance. It is called *oxygen*, and under this name will form the subject of the next chapter.

11. If oxygen be not air itself, but only a constituent of air, it follows that air must have other constituents, or at least one other constituent. If mercury be heated for a long time in contact with a certain confined portion of air, it will abstract from this air all of the oxygen, and there will be left a gas differing from both oxygen and common air. It is unfit for the support of combustion and of animal life; a candle is instantly extinguished by it, as if plunged in water; and small animals, thrust into the gas, die in a few seconds. This gas consists for the most part of a second elementary substance, distinguished by marked chemical and physical peculiarities. It is called *nitrogen*, and under this name will be more completely studied in another chapter.

If the experiment be so conducted that the bulk of the original air, and also that of the residual gas, can be measured, it will be found that the latter occupies four fifths as much space as the air did in the beginning. Beside oxygen and nitrogen, small quantities of certain other gases are found in the air, either uniformly or occasionally; but the amount of these gases is relatively small and they need not be considered at present.

The air, then, is not an element, but a *complex* substance; and its two principal ingredients are the elementary bodies *oxygen* and *nitrogen*, mixed in the proportion of nearly four volumes of nitrogen to one of oxygen. Under great pressure at a very low temperature, air has been obtained in the form of a liquid which on freezing forms a solid ice. (See note, p. 394a.)

CHAPTER II.

OXYGEN.

12. **Oxygen** gas may be obtained, as has already been seen, by heating mercuric oxide. It may, however, be prepared in a variety of ways; among others, and very conveniently, by heating a mixture of potassium chlorate and manganese dioxide, — two chemical substances whose constitution will be studied hereafter.

Exp. 4. — Mix intimately 5 g. of potassium chlorate with 5 g. of “black oxide of manganese,” which has previously been well dried. Place the mixture in a tube of hard glass (No. 1) 12 or 15 cm. in length. Attach to this ignition tube, by means of a perforated cork or caoutchouc stopper, a delivery tube of glass (No. 7), as represented in Fig. 2, and described in Exp. 3, § 9. Heat the mixture in the ignition tube, and collect the gas which will be given off, in bottles or jars of the capacity of about 250 cc. The first 100 cc. or so of gas should be rejected, since it will be contaminated with the air originally contained in the apparatus.

In performing this experiment the following precautions should be observed: 1. Both the potassium chlorate and the manganese dioxide should be perfectly dry and pure, that is, free from moisture, dust, or particles of organic matter; 2. As soon as the oxygen begins to be delivered, the heat beneath the ignition tube should be diminished, if need be, and so regulated that the evolution of gas shall be tranquil and uniform; 3. The uppermost portions of the mixture should be heated before the lower; 4. The ignition tube should never be filled to more than one third its total capacity, lest particles of solid matter be projected into the delivery tube, and the outlet for the gas be thus stopped; 5. The ignition tube should always be inclined as represented in Fig. 2, and never placed upright in the flame.

13. **Oxygen** is a transparent and colorless gas, not to be distinguished by its aspect from atmospheric air. Like air, it has neither taste nor smell. It is, however, somewhat heavier than air. If the weight of a volume of air be taken as 1, then the weight of the same volume of oxygen, measured under the

same conditions of temperature and pressure, is found to be 1.1056. A liter of oxygen under a pressure of 760 mm., and at a temperature of 0° , weighs 1.4298 g. It is but slightly soluble in water, 100 volumes of water at 0° dissolving 4.3 volumes of oxygen. It has been condensed to a colorless transparent liquid by the application of great pressure at a very low temperature, but has not yet been obtained in the solid state. One of the most striking characteristics of oxygen is its power of making things burn. This has been already illustrated in Exp. 3, § 9.

If a piece of phosphorus the size of a small pea, having been well dried between pieces of blotting paper, is placed in a deflagrating spoon, touched with a hot wire or a lighted match, and then thrust into a jar of oxygen, it will burn with intense brilliancy, and with the formation of a dense white smoke. The following experiments will still further illustrate this property of oxygen:—

Exp. 5.—Place in a deflagrating spoon (Appendix, § 13) a bit of sulphur as large as a pea. Light the sulphur, and thrust it into a bottle of oxygen. It will burn with a beautiful blue flame, and much more brilliantly than in air. A suffocating gas is at the same time produced.



Fig. 3.

Exp. 6.—Place a piece of charcoal—that of bark is best—in a deflagrating spoon. Kindle the charcoal by holding it in the flame of a lamp, and then introduce it into a bottle of oxygen. It will burn vividly, throwing off brilliant sparks if bark charcoal has been employed. In this experiment, as in the preceding, the products of the combustion are obviously gaseous, no solid substance being formed.

Many substances commonly called incombustible because they do not burn readily in ordinary air, burn vigorously in oxygen. Of these, metallic iron may be taken as an example. A watch spring, which has been rendered flexible by igniting it and allowing it to cool slowly, is made into a spiral coil, and to the end is attached a bit of tinder, or of twine soaked in sulphur. If the kindling material be lighted, and the spiral then plunged into a jar of oxygen, the iron will burn brilliantly with scintillation. From time to time glowing balls of molten matter fall off from the wire, and bury themselves in the layer of sand which should have been placed at the bottom of the bottle.



Fig. 4.

14. It is thus clearly proved that iron, when red-hot, combines with oxygen. It is the burnt or *oxidized* iron which falls in globules to the bottom of the bottle. The compounds which are formed by the union of oxygen with other elements are called *oxides*. The substances which have been heretofore mentioned under the more familiar name of *rust*, like iron rust, tin rust, mercury rust, are called, in chemistry, *oxides*; as iron oxide, tin oxide, mercury oxide.

15. Oxygen is the most widely diffused and the most abundant of all known substances. Not only does it constitute about one fifth the volume of the air, but at least one third of the solid crust of the globe is composed of it. It is the chief ingredient of water, as will appear in a subsequent chapter. Silica, in all its varieties of sand, flint, quartz, rock crystal, etc., contains about half its weight of oxygen; and the same is true of the various kinds of clay, and of chalk, limestone, and marble. It enters largely into the composition of plants and animals, and is absolutely essential to the maintenance of animal and vegetable life.

16. The most important chemical property of oxygen is, that, with a single exception, it forms compounds with all the other elements. At ordinary temperatures, it does not act readily upon many substances; but at high temperatures, action is exceedingly energetic, and is generally accompanied by the development of light and heat. The light and heat are results of the chemical action. Most of the ordinary phenomena of fire and light which we daily witness depend upon the union of the body burned with the oxygen of the air. All the ordinary processes of *combustion* are processes of oxidation. In the broadest sense of the term, *combustion is chemical combination accompanied by light and heat*. An illustration of the use of the term is seen in Exp. 1, § 2, where the combination of the sulphur and copper causes the mass to glow.

If a substance combines slowly with oxygen, it may often happen that heat cannot be detected. Thus, when iron rusts on exposure to the air, neither light nor heat is noticed, though a combination of iron and oxygen takes place. There is no difference in the total amount of heat produced when a substance burns, and when it undergoes slow oxidation without the evolution of light. In the one case all the heat

produced by the act of combining is given off in a short space of time, and the substance is heated to such a high temperature, that it emits light; in the other, the heat is given off so slowly, that the surrounding substances conduct away the heat as rapidly as it is evolved. If, however, we were to measure the total amount of heat, we would find it to be the same in both cases. Chemical combination is invariably accompanied by an evolution of heat, though in many instances it can be detected only by using the most delicate instruments.

CHAPTER III.

NITROGEN.

17. The simplest method of preparing **nitrogen** is to burn out the oxygen from a confined portion of air by phosphorus or by a jet of hydrogen.

Exp. 7. — Into a small porcelain capsule, supported on a piece of stout iron wire bent as represented in Fig. 5, put about a cubic centimeter of phosphorus, and set it on fire. Invert over the capsule a wide-mouthed bottle, of the capacity of a liter or more, and hold this bottle so that its mouth shall dip beneath the surface of the water. During the first moments of the combustion, the heat developed thereby will cause the air within the bottle to expand to such an extent, that a few bubbles of the air will be expelled; but, after several seconds,



Fig. 5.

water will rise into the bottle to take the place of the oxygen, which has united with the phosphorus.

The dense white cloud which at first fills the bottle is a compound of phosphorus and oxygen, which is soluble in water. It will therefore soon be absorbed by the water in the pan, and will disappear, so that at the close of the experiment nearly pure nitrogen will be left in the bottle; but, as the phosphorus ceases to burn before the last traces of oxygen are exhausted, the nitrogen obtained by this method is never absolutely pure.

Remove the wire with the capsule, which may be readily done by

tipping the bottle to one side, taking care that the mouth does not come out of the water, and slip a glass plate under the mouth of the bottle. Invert the bottle so that it stands upright, and thrust a burning splinter of wood or a lighted candle into the gas: it will be instantly extinguished.

Nitrogen may also be prepared by passing a slow stream of air over bright copper turnings heated to redness in a hard-glass tube. The copper combines with the oxygen of the air, and retains it; while the nitrogen escapes from the tube, and may be collected over water.

18. Nitrogen is a transparent, colorless, tasteless, odorless gas, not quite as heavy as air. A liter of nitrogen at 0°, and 760 mm. pressure, weighs 1.255 g. It has been obtained in the form of a colorless liquid by subjecting it to very low temperature and great pressure. The liquid solidifies at -214°. In its chemical deportment towards other substances, it is remarkably unlike oxygen. Whilst oxygen is active, and, as it were, aggressive, nitrogen, at least when in the condition in which it exists in air, is remarkably inert and indifferent as regards entering into combination with other bodies. It is marked rather by the absence of salient characteristics than by any active properties of its own.

As it extinguishes flames, so it destroys life. Animals cannot live in an atmosphere of pure nitrogen. It is not poisonous: if it were, it could not be breathed in such large quantities as it is in air. An animal immersed in it dies simply from want of oxygen. In the air it serves the useful purpose of diluting the oxygen.

Nitrogen is widely diffused in nature. Beside occurring free in the air, of which it constitutes nearly four fifths of the volume, it is a constituent part of all forms of animal and vegetable life, and of many of the products resulting from the decomposition of animals and plants. Notwithstanding the indisposition of nitrogen in the free state to enter into combination, a very large number of interesting and important compounds can be formed by resorting to indirect methods of effecting its union with other elements.

19. In connection with many chemical investigations, it is necessary to consider the comparative weights and volumes of substances in the gaseous condition. The chief difficulty encountered in making such

comparisons is due to the fact that the volumes of gases vary under different conditions of temperature and pressure. A given volume of nitrogen, a liter of the gas for instance, will weigh less at a temperature of 100° than a liter of the same gas measured and weighed at 0° . Since the volume of a gas increases with the temperature, and diminishes with the pressure to which it is subjected, it is necessary to adopt some *standard* conditions in order to make useful comparisons. The normal, or standard, temperature adopted is 0° Centigrade. The standard pressure is indicated by the pressure necessary to support a column of mercury 760 mm. high (§ 7). Volumes of gases are always compared under these standard conditions of temperature and pressure; and, when measurements are made under other conditions, it is customary to reduce the volumes obtained to these standards.

It has been found, that, for each increase of 1° Centigrade of temperature, the volume of a gas measured at 0° will expand to the extent of $\frac{1}{273}$, or, when expressed as a decimal fraction, to the extent of 0.00366, of its bulk. For example: 1 cc. of any gas at 0° becomes at 1° , $1\frac{1}{273}$ cc.; at 2° , $1\frac{2}{273}$ cc.; at 100° , $1\frac{100}{273}$ cc.; at 273° , 2 cc.; for it is a fact of experiment, formulated in the statement known as the **Law of Charles**, that *all true gases, when heated, expand $\frac{1}{273}$ of their volume, measured at 0° Centigrade, for each increase of 1° Centigrade.*

If V_0 represent the volume of a gas when measured at 0° , and T represent any other temperature at which the gas may have been measured, then the volume of the gas at this temperature (V_t) may be expressed by the equations $V_t = V_0 + \frac{T}{273} V_0$ and $V_t = V_0 (1 +$

0.00366 $T)$. So, too, conversely, $V_0 = \frac{V_t}{1 + 0.00366 T}$. The changes

in the volume of a gas due to pressure are governed by **Boyle's Law**, that *the volume of a gas varies inversely as the pressure*. In other words, if the pressure to which a given volume of a gas is subjected is doubled, the volume decreases by one half; and, if the pressure is decreased by one half, the volume is doubled. If a gas has the volume V under a pressure P , and the volume V_1 under the pressure P_1 , then the two values will bear to each other the relation expressed in the proportion, $V : V_1 = P_1 : P$. The pressure is usually stated in millimeters of mercury, and is learned from the barometer. The two corrections may be made at once; and a volume measured at any temperature and under any pressure can be reduced to standard conditions, or conversely, by the

use of the formula $V_{0^{\circ}+760 \text{ mm.}} = \frac{V_t P}{760 (1 + 0.00366 T)}$, in which $V_{0^{\circ}+760}$ is the volume under standard conditions, V_t the observed volume, T the observed temperature, and P the observed pressure.

CHAPTER IV.

WATER.

20. Another natural substance, quite as common as air, is **water**. Three fourths of the earth's surface is covered with it. It is diffused through the atmosphere in the form of vapor, and is a constituent of all animal and vegetable substances and of many minerals. We proceed to study this familiar substance, in order that we may gain a deeper insight into chemical principles, and enlarge our experience by making acquaintance with a new element.

21. At the ordinary temperature of the air, pure water is a transparent liquid, devoid of taste or smell. In thin layers, it appears to be colorless; but large masses of it are distinctly blue, as seen in mid-ocean, in many deep lakes of pure water, and in masses of ice, such as compact icebergs, and some glaciers where it is possible to look through the ice from below.

22. At 4°, the temperature at which it is densest, water is 773 times heavier than air at 0°. A cubic centimeter of water at this temperature, weighed in a vacuum, is our unit of weight, — a *gram*: therefore one liter of water, which measures 1000 cc., weighs a kilogram.

Pure water is taken as a standard to which the weights of equal bulks of other substances, liquid or solid, are referred: that is to say, the *specific gravity* of water at 4° is taken as 1; and in terms of this unit the specific gravities of all other liquid and solid substances are expressed, the **specific gravity** of a body being the relation between the weight of a given bulk of the body and the weight of the same bulk of water at 4°. The specific gravity of gold, for example, is 19.3; that is to say, the weights of equal bulks of water and of gold are to each other as 1 to 19.3. Since in the metric system (Appendix, § 29) the unit of weight is the weight of the

unit of volume of water at 4°, it is always true that the *volume* of a body equals its *weight* divided by the *specific gravity*.

$$V = W \div \text{Sp. Gr.}, \text{ and } W = V \times \text{Sp. Gr.}$$

Water is also the standard of *specific heat*. The specific heat of a body is the amount of heat required to raise the temperature of a certain weight of that substance 1°, while the amount required to raise the temperature of an equal weight of water 1° is taken as unity. In measuring heat from any source, it is customary to determine how many grams of water can be raised 1° in temperature by means of it. The term *calorie*, usually abbreviated to *cal.*, is employed to designate the quantity of heat required to raise the temperature of 1 g. of water 1° Centigrade. Thus, the statement "300 cal." indicates a quantity of heat capable of raising the temperature of 300 g. of water 1° Centigrade.¹ It should be said, however, that, although the definition here given is approximately correct, it is not absolutely so, for the specific heat of water varies slightly at different temperatures, more heat being required to raise the temperature of 1 g. of water from 99° to 100° than from 0° to 1°. Hence the unit or calorie generally accepted is the one-hundredth part of the quantity of heat required to raise the temperature of 1 g. of water from 0° to 100°. This amount coincides very nearly with that needed to raise the temperature of 1 g. of water from 15.5° to 16.5°.

23. When exposed to a certain degree of cold, water *crystallizes*, with formation of ice or snow, according to circumstances; and, upon being heated sufficiently, it is transformed into an invisible gas, called *steam*. Both these changes, however, are purely physical: the chemical composition of the water is the same, whether it be liquid, solid, or gaseous. The temperature at which ice melts is one of the fixed points of the Centigrade thermometer, numbered 0°; and the temperature at which water boils, under a pressure of 760 mm. of mercury, is the other fixed point, numbered 100°. Water evaporates at all temperatures, and is therefore a constant ingredient of the atmosphere. Even ice slowly evaporates, at temperatures far below 0°, without first passing into the liquid condition.

In crystallizing, that is to say, in assuming the solid form, water increases in volume. From this fact result many familiar

¹ The English term *thermal unit* differs from the French term *calorie* in that it notes the quantity of heat required to raise one pound of water ten degrees of Fahrenheit's thermometer.

phenomena, such as the floating of ice, the upheaving and disintegrating action of frost, and the bursting of pipes and other hollow vessels when water is frozen in them.

24. **Steam** is a colorless, transparent gas, as invisible as atmospheric air, and considerably lighter than it. When steam escapes into the air, it is partly condensed to the liquid state, and there is formed a multitude of little globules precisely similar to the minute drops of water which make up ordinary clouds and fogs. This steam cloud is sometimes improperly spoken of as steam or vapor, an error against which the student should be on his guard. Similar fogs are formed whenever the atmosphere is cooled to a temperature so low that the aqueous vapor contained in it can no longer exist in the gaseous state.

Water conducts heat very slowly; it may even be boiled for many minutes at the top of a test tube, while the lower end of the tube is held in the fingers without inconvenience.

25. Let us now pass to the analysis of water. Of what is water composed? We can determine this point by methods similar to those which were adopted in the examination of air. At a low red heat, water can be decomposed by several of the metals, such as iron, tin, zinc, and magnesium. Iron is well adapted for this purpose.

If water be boiled in a suitable flask, and the steam passed through an iron tube (a piece of iron gas pipe answers very well) filled with bright iron turnings, and heated red-hot, the steam is decomposed. A gas escapes from the tube, and may be collected over water. On the application of a match, the gas will burn with a pale blue flame. This gas is one of the constituents of water, and is called *hydrogen*. If, after the tube has become cold, the iron turnings be removed, they will be found to be covered with a black coating similar to that which forms on iron heated in the air.

26. There are certain metals capable of decomposing water without the application of heat. The metal sodium possesses this power.

Exp. 8. — Make a small cylinder of wire gauze by rolling a piece of fine gauze, about 6 cm. square, around a thick piece of No. 6 glass tubing. Twist fine wire around the cylinder, in order to preserve its form; then slip the cylinder off the glass, and close one end of it by

pressure with a stout pair of pincers. Within this cylinder of wire gauze place a piece of metallic sodium as large as a pea, and then close the upper end of the cylinder by pressure with the pincers, as before.



Fig. 6.

Attach the wire-gauze cage firmly to the end of a piece of stout iron wire, and thrust it quickly into the water pan, so that the cage will come directly under the mouth of a small bottle, of about 100 cc. capacity, which has been previously filled with water, and is held inverted in the pan (Fig. 6).

As soon as the water comes in contact with the sodium, bubbles of gas will begin to escape from the wire-gauze cage, and, passing up through the water, will collect at the top of the inverted bottle. When the evolution of gas has ceased, close the mouth of the bottle with a small plate of glass, turn the bottle mouth uppermost, remove the plate, and touch a lighted match to the gas. The gas will take fire with a sudden flash. The gas is hydrogen. The sodium has united with the other constituent (or constituents) of the portion of water decomposed, and the new compound formed is dissolved by the water in the pan. The yellow color of the flame is due to the presence of some sodium. Pure hydrogen burns with a pale blue, almost invisible flame.

27. By these experiments it has been proved that one of the components of water is a gas called *hydrogen*; but, with the exception of the coating upon the iron alluded to in § 25, we have as yet nothing to indicate what other ingredients the water may contain. Such evidence can, however, be readily obtained by resorting to another method of analysis.

If an electric current is caused to flow through water, the force by which the constituents of the water are held together will be overcome, and the water will be resolved into the elements of which it is composed. On immersing the platinum poles of a galvanic battery in water to which a little sulphuric acid has been added for the purpose of increasing its conducting power, minute bubbles of gas will immediately be given off from these poles attached to the terminal wires, and will be seen rising through the liquid. If the apparatus be so arranged that we can collect the gas given off from each pole in a tube filled with water to which a little sulphuric acid has been added, it will be found that twice as much gas has collected in the one tube as in the other. If the tube containing the larger volume of gas

be now closed with the thumb, turned mouth uppermost, and the gas within touched with a lighted match, it will take fire, and burn with the characteristic flame of hydrogen. It is, in fact, hydrogen. If the smaller volume of gas in the other tube be examined in the same way, it will not inflame, although it gives intense brilliancy to the combustion of the match. If a splinter of wood, retaining but a single ignited spark, be immersed in the gas, it instantly exhibits a vivid incandescence, and in a moment bursts into flame. This gas is oxygen.

It is thus proved by *electrolysis* that two volumes of hydrogen and one volume of oxygen may be set free from water. It remains to be seen whether we can produce water from a mixture of oxygen and hydrogen.

If we introduce into a small, stout tube a mixture of two volumes of hydrogen and one volume of oxygen, and touch a lighted match to the mixed gas, it instantly explodes with great violence, the hydrogen burning suddenly, so that for a moment a flash of flame fills the whole interior of the tube. After the explosion, water will be found deposited as dew upon the inner walls of the tube.



Fig. 7.

28. We have thus established the composition of water by *analysis*, having resolved water into two gaseous constituents, hydrogen and oxygen; we have also proved, by the converse or *synthetical* method, that hydrogen and oxygen are its only constituents, since we have reproduced water by effecting the chemical union of these two elementary materials mixed in due proportion.

This proportion is fixed and invariable. Pure water is always made up of hydrogen and oxygen in the proportion of two volumes of the former for one of the latter. From the known specific gravities of the two gases, as well as by direct experiment, the composition of water *by weight* has been found to be 1 part by weight of hydrogen to very nearly 8 parts by

It is not improbable, that, in all cases of the solution of solids in water, actual but unstable compounds of water and the dissolved substances are formed. In some cases, indeed, such compounds have been obtained.

Many compounds, when obtained in the form of crystals by deposition from their solution in water, are found to be combined with definite quantities of water. This so-called *water of crystallization* is not directly visible to the eye. Solids that contain it do not appear to be moist, nor can any water be felt on touching them; but it is none the less true that the water thus held in combination is often essential to the crystalline form of the substance, and sometimes to its color also. Water of crystallization may generally be driven off by heating the crystals to 100° , when they commonly crumble to powder and lose their transparency or color.

Exp. 14. — Heat gently a crystal of copper sulphate in a test tube until no more steam passes off. When cool, add a few drops of water to the whitish substance obtained.

In the case of some substances, simple contact with the air causes loss of water of crystallization. Such bodies are said to be *efflorescent*. Some compounds, if deprived of their water of crystallization, will take it on again when exposed to moist air. Substances which become wet by absorbing moisture from the air are said to be *deliquescent*.

Exp. 15. — Put some clear crystals of common Glauber's salt, sodium sulphate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), on a plate, and leave them exposed to the air for an hour or more. The crystals will gradually become white, and finally crumble to a white powder. In the same way expose a few bits of calcium chloride (CaCl_2) to the air. If left for a sufficient time, the substance will absorb so much moisture as to actually dissolve, and thus assume a liquid condition.

Of the various substances soluble in water, some dissolve in far larger proportion than others. With some liquids, as alcohol for example, water can be mixed in any proportion; but of ether it dissolves but little, and of oil next to none. The proportion of any substance that can be dissolved in a given quantity of water is usually limited, and, under fixed conditions, is definite and peculiar for each substance. When a given quantity of water has dissolved as much of a substance as it is capable of dissolving at the temperature and pressure

to which it happens to be exposed, the solution is said to be *saturated*.

At a temperature of 60°, 100 cc. of water will dissolve 110 g. of potassium nitrate (saltpeter), forming a saturated solution, for at this temperature 100 cc. of water are incapable of dissolving any more of the solid. If the solution be allowed to cool to, say, 20°, a certain amount of the potassium nitrate will separate from the solution, 100 cc. of water at 20° being capable of dissolving only about 32 g. of the solid. It is, however, often possible to obtain what are called *supersaturated* solutions by preparing a saturated solution at a high temperature, and allowing the liquid to cool slowly in a quiet place. With many salts, if a hot, saturated solution be allowed to cool without agitation, it happens that the liquid will still retain, when cold, more of the salt than it could have dissolved outright at the lower temperature.

Exp. 16. — Heat in a clean glass flask 100 cc. of water to which 200 g. of crystallized sodium sulphate (Glauber's salt) have been added. As soon as complete solution takes place, cork the flask and allow it to cool. When cold, remove the cork, and shake the flask, or stir the contents with a glass rod which has been left lying for some time in the air. At a temperature of 33°, water dissolves about half its own weight of crystallized sodium sulphate; and if the solution be protected from dust, and allowed to cool quietly to the ordinary temperature of the air, the whole of the substance will remain in solution. If, however, a small crystal of the sodium sulphate be dropped into the solution, the whole mass will immediately become solid. Solidification does not occur on touching the solution with a rod freed from dust by ignition, or by soaking the rod in sulphuric acid and washing and drying it in air free from dust.

Exp. 17. — In a clean round-bottomed flask of about 350 cc. capacity place 50 cc. of water, and, while warming the water gently, add gradually 300 g. of sodium thiosulphate (hyposulphite of soda). When the sodium thiosulphate has dissolved, bring the mixture to a boil, close the mouth of the flask with a plug of cotton wool, and allow the liquid to cool. When cold, the solution will be so concentrated as to have an oily consistency. The flask may be carefully uncorked, and the surface of the liquid touched with a glass rod to the end of which a small particle of the sodium thiosulphate has been made to adhere. Crystallization at once takes place, and considerable heat is developed.

Of nearly all solid substances, hot water dissolves a greater quantity than cold water; gases, however, are less soluble in hot than in cold water, as already illustrated by Exp. 11, § 35.

Many compounds, when exposed from their solution with definite quantities of crystallization is not dissolved. When it do not appear to be touching them; but it is thus held in combination in form of the substance, and of crystallization may generate crystals to 100°, when they lose their transparency or color.

In the case of some substances, loss of water of crystallization. Some compounds, if dried, can be wet again when wet by absorbing

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This experiment, which has here been executed with zinc, can be equally well performed with iron filings, and with several other of the less common metals.

38. We now proceed to study the chemical action which takes place in the above experiment. The *muratic acid* as it is commonly termed, or, in chemical language, *hydrochloric acid*, which was employed, is in reality a solution in water of a very soluble gaseous substance, to which the name *hydrochloric acid* is more strictly applied. This gaseous substance, the pure hydrochloric acid, is a chemical compound of the element hydrogen and of another element, called *chlorine*, which will shortly be described. The compound may be represented by the symbol HCl , in which H represents, as before, the least proportional weight of hydrogen which exists in combination, and Cl the least proportional weight of chlorine. We may also abbreviate the word *zinc* to the symbol Zn ; and the chemical process, or *reaction*, by which the hydrogen is liberated, may then be symbolized by the equation —



When zinc is mixed with the acid, as such, and there remains no hydrogen, the bottle contains a compound of the zinc and chlorine, called *zinc chloride*. The zinc, in this combination, and the hydrogen, which is set free; in other words, the hydrogen, has been *replaced*, or has *replaced*, the hydrogen.

Chemists of all nations have agreed to represent each element by a symbol, which consists usually of

CHAPTER V.

HYDROGEN.

37. The commonest method of preparing **hydrogen** is by treating zinc or iron with sulphuric or hydrochloric acid. This method is much more convenient than either of those heretofore mentioned.

Exp. 18.—To a bottle 18 or 20 cm. high, and of 500 or 600 cc. capacity, the mouth of which has an internal diameter of 2.5 to



Fig. 9.

3 cm., fit a caoutchouc stopper or a sound cork, furnished with a thistle tube (Fig. 9) and a gas delivery tube of No. 6 glass. Within the bottle put 15 or 20 g. of granulated zinc, or small scraps of the sheet metal, and as much water as will fill about one quarter of the bottle. Replace the cork in the bottle, taking care to press it in tightly, and gradually pour in common hydrochloric acid through the thistle tube. The thistle tube must reach nearly to the bot-

tom of the bottle, so that its point may dip beneath the water; and the hydrochloric acid must be added by small successive portions,—not more than a large thimbleful at a time.

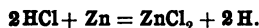
On the addition of the first portions of the acid, chemical action will ensue, the contents of the bottle will become warm, and gas will be seen to escape from the liquid. This gas is hydrogen.

After all the air has been expelled from the bottle, the hydrogen may be collected over the water pan, in inverted bottles filled with water. The moment at which the hydrogen ceases to be contaminated with air can be determined by collecting small portions of the escaping gas in wide-mouthed bottles of about 50 cc. capacity, and testing its quality by means of a lighted match. In doing this, the small bottle filled with gas must not be turned over, but should be carefully

lifted from the water without changing its vertical position, and the lighted match should then be applied to the mouth of the bottle. If the hydrogen be pure, it will burn tranquilly at the mouth of and within the bottle; but, in case the gas is still mixed with much air, a sharp explosion will occur at the moment when the match is touched to it. In experimenting with hydrogen, no light should ever be brought into contact with the contents of the bottle in which it is generated, or with any large quantity of the gas, until the purity of the sample, or rather its nonexplosive character, has been demonstrated by applying to a very small volume of the gas the test above described. The hydrogen thus prepared has a faint odor due to a slight admixture of foreign substances. The pure gas is odorless.

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Since hydrogen is a gas, it escapes as such, and there remains dissolved in the water within the bottle a compound of the elements chlorine and zinc, called *zinc chloride*. The zinc, which was free, enters into combination, and the hydrogen, which was in combination, is set free; in other words, the zinc has been *substituted* for, or has *replaced*, the hydrogen.

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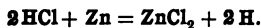


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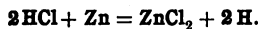
On the addition of the first portions of the acid, chemical action will ensue, the contents of the bottle will become warm, and gas will be seen to escape from the liquid. This gas is hydrogen.

After all the air has been expelled from the bottle, the hydrogen may be collected over the water pan, in inverted bottles filled with water. The moment at which the hydrogen ceases to be contaminated with air can be determined by collecting small portions of the escaping gas in wide-mouthed bottles of about 50 cc. capacity, and testing its quality by means of a lighted match. In doing this, the small bottle filled with gas must not be turned over, but should be carefully

lifted from the water without changing its vertical position, and the lighted match should then be applied to the mouth of the bottle. If the hydrogen be pure, it will burn tranquilly at the mouth of and within the bottle; but, in case the gas is still mixed with much air, a sharp explosion will occur at the moment when the match is touched to it. In experimenting with hydrogen, no light should ever be brought into contact with the contents of the bottle in which it is generated, or with any large quantity of the gas, until the purity of the sample, or rather its nonexplosive character, has been demonstrated by applying to a very small volume of the gas the test above described. The hydrogen thus prepared has a faint odor due to a slight admixture of foreign substances. The pure gas is odorless.

This experiment, which has here been executed with zinc, can be equally well performed with iron filings, and with several other of the less common metals.

38. We now proceed to study the chemical action which takes place in the above experiment. The *muratic acid* as it is commonly termed, or, in chemical language, *hydrochloric acid*, which was employed, is in reality a solution in water of a very soluble gaseous substance, to which the name *hydrochloric acid* is more strictly applied. This gaseous substance, the pure hydrochloric acid, is a chemical compound of the element hydrogen and of another element, called *chlorine*, which will shortly be described. The compound may be represented by the symbol HCl , in which H represents, as before, the least proportional weight of hydrogen which exists in combination, and Cl the least proportional weight of chlorine. We may likewise abbreviate the word *zinc* to the symbol Zn ; and the chemical process, or *reaction*, by which the hydrogen is liberated, may then be symbolized by the equation —



Since hydrogen is a gas, it escapes as such, and there remains dissolved in the water within the bottle a compound of the elements chlorine and zinc, called *zinc chloride*. The zinc, which was free, enters into combination, and the hydrogen, which was in combination, is set free; in other words, the zinc has been *substituted* for, or has *replaced*, the hydrogen.

It may here be stated that chemists of all nations have agreed to represent each of the elements by a symbol, which consists usually of

is made up of two atoms of hydrogen and one atom of oxygen, the proportion by weight in which these two elements are combined will be as 2 to 16, or as 1 to 8.

31. Having thus succeeded in determining the constituents of air and water, we are naturally led to inquire whether it be not possible to resolve oxygen, nitrogen, and hydrogen themselves into simpler forms of matter. To this question but one answer can be made; namely, that oxygen, nitrogen, and hydrogen are incapable of decomposition by any means as yet at our disposal. We are therefore justified in regarding these gases as *simple* bodies, or *elements*, in contradistinction to decomposable bodies, such as water.

32. The water which occurs in nature is never absolutely pure. In the form of ice, and as it falls from the clouds as rain or snow, it is, indeed, tolerably free from foreign substances; but, after having once soaked into the ground, it becomes charged with a variety of mineral and other substances, which, being soluble in water, are dissolved by it as it trickles through the earth.

Where the proportion of soluble matter contained in the water is unusually large, and particularly if it possesses marked medicinal properties, the water is called *mineral water*, and the springs from which it issues are known as *mineral springs*. Sea water may be regarded as a variety of mineral water.

33. For the conduct of chemical investigations, it is often necessary to purify natural water. This is done by a process called *distillation*. As a general rule, distilled water is employed in all delicate chemical operations.

Exp. 9. — In a retort of 500 cc. capacity, put 200 or 300 cc. of well water. Thrust the neck of the retort into a half-liter receiver placed in a pan of cold water. Cover the receiver with a cloth or with coarse paper, and upon this pour cold water from time to time, or pile upon it fragments of ice. Place the retort upon wire gauze, on a ring of the iron lamp stand, and adjust the distance of the retort from the lamp as described in Exp. 3, Fig. 2. Light the lamp beneath the retort, and bring the water to boiling. As fast as the water in the retort is converted into steam, this vapor will pass over into the cold receiver, and will there be condensed again to the liquid condition.

Continue to boil until about three quarters of the water in the retort has evaporated.

The earthy and saline ingredients of well water are for the most part not volatile: very few of them are capable of accompanying the water as it goes off in vapor; hence the greater part of the original impurity of the water will remain behind in the retort.

Exp. 10. — Place a few drops of the distilled water obtained in the preceding experiment upon a piece of platinum foil (Appendix, § 14). Hold the foil with iron pincers above the gas flame in such a manner that the liquid may slowly evaporate without boiling or spirting. After the water has disappeared, no residue will be found upon the foil. Take now the same number of drops of water from out the retort, and evaporate them upon the foil as before. A very decided residue of earthy matter will be left upon the foil.

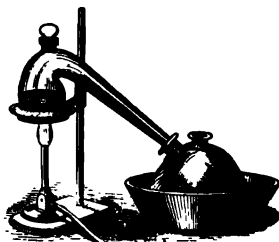


Fig. 8.

34. In the operation of **distillation**, the substance to be distilled must in the first place be converted into the condition of vapor. This vapor must next be transferred to another vessel, and there, by refrigeration, be again condensed to the liquid state. As will appear from the foregoing experiment, the vaporization is effected in the *retort* or *still*, and the refrigeration in the *condenser*. In the experiment above given, the receiver acts at once as receiver and condenser; but in many cases it is better to interpose a cooling apparatus between the retort and the receiver. A convenient form of such apparatus is arranged so that the vapor to be condensed must pass into a long tube, which is kept cool by being inclosed in a larger tube through which cold water is made to circulate. A figure representing such a condenser will be found in § 294.

35. The mineral and other substances alluded to above are not the only impurities of natural water. It contains also oxygen and nitrogen in solution, as both of these gases, which are present in the air, are somewhat soluble in water. That water does actually contain dissolved gases in appreciable quantities, and that these gases can be expelled by heating the water, may be shown by the following experiment.

Exp. 11.—By means of a sound perforated cork or caoutchouc stopper, adapt to a flask of the capacity of 1 or 2 l. a gas delivery tube (No. 6) long enough to reach to the water pan in the usual way. Upon the outer end of the delivery tube tie a short piece of caoutchouc tubing to which a stopper made of a bit of glass rod, or a wooden plug, has been fitted. Fill the flask completely with ordinary well or river water; fill also the delivery tube with water, and close it by putting the stopper in the caoutchouc tube. Carefully place the cork of the delivery tube in the neck of the flask in such manner that no air shall be entangled by the cork; at the same moment remove the plug from the delivery tube, and finally press the cork firmly into the flask. Both flask and tube will now be completely full of water. Place the dried flask upon wire gauze or asbestos paper on a ring of the iron stand, and invert a bottle filled with water over the end of the delivery tube. Now slowly bring the contents of the flask to boiling.

As the water gradually becomes warm, numerous little bubbles of gas will be seen to separate from the liquid, and to collect upon the sides of the flask; the gases present being less soluble in hot than in cold water. They subsequently coalesce to larger bubbles, which collect in the neck of the flask. As soon as the water actually boils, the steam will force this gas out of the flask, and it will collect in the inverted bottle at the end of the delivery tube, the steam being meanwhile condensed as fast as it comes in contact with the cold water in the pan. By continuing to boil moderately during ten or fifteen minutes, nearly all the gas can be swept out from the flask by means of the escaping steam. The delivery tube may then be lifted from the water pan, and the lamp extinguished. As to the exact character of the gases thus collected, we shall learn something in a subsequent chapter.

36. As might be inferred from the foregoing, water has the property of dissoiving many substances, solid, liquid, and gaseous. Sugar, for example, dissolves readily in water; but sand is insoluble therein. A substance is said to be soluble in water when it is capable of being divided in and dispersed through the water so intimately and completely that its particles become invisible, and can no longer be separated by filtration; that is, by passing through a porous medium. The result of this coalescence, or the *solution*, as it is termed, is a transparent liquid (unless the body dissolved be strongly colored, when its transparency may be diminished), as a general rule scarcely less mobile than the water itself. The ultimate particles of the substance, i.e., its molecules, are no longer held together by

the attraction called *cohesion*, which holds molecules of the same kind together, but have become separated, and uniformly distributed among the molecules of the water. The extent to which this uniform distribution of the particles of the dissolved substance takes place can be seen by dissolving in a large amount of water a small particle of the dyestuff called *fuchsin*. If some pure table salt be dissolved in water, the result is simply a mixture, so far as can be perceived. No chemical change in the dissolved substance can be detected, and there is no evidence that chemical action has taken place between the salt and the water. If the solution thus obtained be evaporated, the water passes off as a vapor, and the salt is recovered unchanged. Such a solution is called a *physical solution*. But if a little sodium carbonate (common washing soda) be treated with hydrochloric acid, evidence of chemical change is noticed; and if, after effervescence has ceased, the liquid obtained be evaporated to dryness, there will remain a substance distinctly different from the sodium carbonate. A solution such as this, where the substance obtained by the evaporation of the liquid used as a solvent differs chemically from the original substance, is a *chemical solution*.

Exp. 12. — Take 2.5 g. of common salt, and dissolve it in 10 cc. of distilled water. Evaporate the solution slowly to dryness, and compare the substance obtained with the original salt as to appearance, taste, and crystalline form. Dissolve 5 g. of sodium carbonate in dilute hydrochloric acid, evaporate the solution, and compare the solid left with the original substance as to appearance and taste and by treating it with dilute hydrochloric acid.

In order that chemical solution may take place, it is essential that the new substance formed be soluble in the liquid present.

Exp. 13. — Place 5 cc. of alcohol in a test tube, add 1 cc. of strong hydrochloric acid, and shake the mixture. Drop a small bit of fused potassium carbonate into the tube. It will be noticed that slight effervescence takes place, which soon ceases, and that a white residue remains undissolved: it is potassium chloride, which is insoluble in strong hydrochloric acid. Place 5 cc. of water in a test tube and add 1 cc. of acid, as before. Drop a small piece of fused potassium carbonate into the tube. In this case no residue remains. Chemical solution has taken place, for the potassium chloride formed is soluble in the water.

It is not improbable, that, in all cases of the solution of solids in water, actual but unstable compounds of water and the dissolved substances are formed. In some cases, indeed, such compounds have been obtained.

Many compounds, when obtained in the form of crystals by deposition from their solution in water, are found to be combined with definite quantities of water. This so-called *water of crystallization* is not directly visible to the eye. Solids that contain it do not appear to be moist, nor can any water be felt on touching them; but it is none the less true that the water thus held in combination is often essential to the crystalline form of the substance, and sometimes to its color also. Water of crystallization may generally be driven off by heating the crystals to 100° , when they commonly crumble to powder and lose their transparency or color.

Exp. 14. — Heat gently a crystal of copper sulphate in a test tube until no more steam passes off. When cool, add a few drops of water to the whitish substance obtained.

In the case of some substances, simple contact with the air causes loss of water of crystallization. Such bodies are said to be *efflorescent*. Some compounds, if deprived of their water of crystallization, will take it on again when exposed to moist air. Substances which become wet by absorbing moisture from the air are said to be *deliquescent*.

Exp. 15. — Put some clear crystals of common Glauber's salt, sodium sulphate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), on a plate, and leave them exposed to the air for an hour or more. The crystals will gradually become white, and finally crumble to a white powder. In the same way expose a few bits of calcium chloride (CaCl_2) to the air. If left for a sufficient time, the substance will absorb so much moisture as to actually dissolve, and thus assume a liquid condition.

Of the various substances soluble in water, some dissolve in far larger proportion than others. With some liquids, as alcohol for example, water can be mixed in any proportion; but of ether it dissolves but little, and of oil next to none. The proportion of any substance that can be dissolved in a given quantity of water is usually limited, and, under fixed conditions, is definite and peculiar for each substance. When a given quantity of water has dissolved as much of a substance as it is capable of dissolving at the temperature and pressure

to which it happens to be exposed, the solution is said to be *saturated*.

At a temperature of 60°, 100 cc. of water will dissolve 110 g. of potassium nitrate (saltpeter), forming a saturated solution, for at this temperature 100 cc. of water are incapable of dissolving any more of the solid. If the solution be allowed to cool to, say, 20°, a certain amount of the potassium nitrate will separate from the solution, 100 cc. of water at 20° being capable of dissolving only about 32 g. of the solid. It is, however, often possible to obtain what are called *supersaturated* solutions by preparing a saturated solution at a high temperature, and allowing the liquid to cool slowly in a quiet place. With many salts, if a hot, saturated solution be allowed to cool without agitation, it happens that the liquid will still retain, when cold, more of the salt than it could have dissolved outright at the lower temperature.

Exp. 16. — Heat in a clean glass flask 100 cc. of water to which 200 g. of crystallized sodium sulphate (Glauber's salt) have been added. As soon as complete solution takes place, cork the flask and allow it to cool. When cold, remove the cork, and shake the flask, or stir the contents with a glass rod which has been left lying for some time in the air. At a temperature of 33°, water dissolves about half its own weight of crystallized sodium sulphate; and if the solution be protected from dust, and allowed to cool quietly to the ordinary temperature of the air, the whole of the substance will remain in solution. If, however, a small crystal of the sodium sulphate be dropped into the solution, the whole mass will immediately become solid. Solidification does not occur on touching the solution with a rod freed from dust by ignition, or by soaking the rod in sulphuric acid and washing and drying it in air free from dust.

Exp. 17. — In a clean round-bottomed flask of about 350 cc. capacity place 50 cc. of water, and, while warming the water gently, add gradually 300 g. of sodium thiosulphate (hyposulphite of soda). When the sodium thiosulphate has dissolved, bring the mixture to a boil, close the mouth of the flask with a plug of cotton wool, and allow the liquid to cool. When cold, the solution will be so concentrated as to have an oily consistency. The flask may be carefully uncorked, and the surface of the liquid touched with a glass rod to the end of which a small particle of the sodium thiosulphate has been made to adhere. Crystallization at once takes place, and considerable heat is developed.

Of nearly all solid substances, hot water dissolves a greater quantity than cold water; gases, however, are less soluble in hot than in cold water, as already illustrated by Exp. 11, § 35.

CHAPTER V.

HYDROGEN.

37. The commonest method of preparing **hydrogen** is by treating zinc or iron with sulphuric or hydrochloric acid. This method is much more convenient than either of those heretofore mentioned.

Exp. 18. — To a bottle 18 or 20 cm. high, and of 500 or 600 cc. capacity, the mouth of which has an internal diameter of 2.5 to



Fig. 9.

3 cm., fit a caoutchouc stopper or a sound cork, furnished with a thistle tube (Fig. 9) and a gas delivery tube of No. 6 glass. Within the bottle put 15 or 20 g. of granulated zinc, or small scraps of the sheet metal, and as much water as will fill about one quarter of the bottle. Replace the cork in the bottle, taking care to press it in tightly, and gradually pour in common hydrochloric acid through the thistle tube. The thistle tube must reach nearly to the bot-

tom of the bottle, so that its point may dip beneath the water; and the hydrochloric acid must be added by small successive portions, — not more than a large thimbleful at a time.

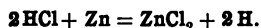
On the addition of the first portions of the acid, chemical action will ensue, the contents of the bottle will become warm, and gas will be seen to escape from the liquid. This gas is hydrogen.

After all the air has been expelled from the bottle, the hydrogen may be collected over the water pan, in inverted bottles filled with water. The moment at which the hydrogen ceases to be contaminated with air can be determined by collecting small portions of the escaping gas in wide-mouthed bottles of about 50 cc. capacity, and testing its quality by means of a lighted match. In doing this, the small bottle filled with gas must not be turned over, but should be carefully

lifted from the water without changing its vertical position, and the lighted match should then be applied to the mouth of the bottle. If the hydrogen be pure, it will burn tranquilly at the mouth of and within the bottle; but, in case the gas is still mixed with much air, a sharp explosion will occur at the moment when the match is touched to it. In experimenting with hydrogen, no light should ever be brought into contact with the contents of the bottle in which it is generated, or with any large quantity of the gas, until the purity of the sample, or rather its nonexplosive character, has been demonstrated by applying to a very small volume of the gas the test above described. The hydrogen thus prepared has a faint odor due to a slight admixture of foreign substances. The pure gas is odorless.

This experiment, which has here been executed with zinc, can be equally well performed with iron filings, and with several other of the less common metals.

38. We now proceed to study the chemical action which takes place in the above experiment. The *muriatic acid* as it is commonly termed, or, in chemical language, *hydrochloric acid*, which was employed, is in reality a solution in water of a very soluble gaseous substance, to which the name *hydrochloric acid* is more strictly applied. This gaseous substance, the pure hydrochloric acid, is a chemical compound of the element hydrogen and of another element, called *chlorine*, which will shortly be described. The compound may be represented by the symbol HCl , in which H represents, as before, the least proportional weight of hydrogen which exists in combination, and Cl the least proportional weight of chlorine. We may likewise abbreviate the word *zinc* to the symbol Zn ; and the chemical process, or *reaction*, by which the hydrogen is liberated, may then be symbolized by the equation —



Since hydrogen is a gas, it escapes as such, and there remains dissolved in the water within the bottle a compound of the elements chlorine and zinc, called *zinc chloride*. The zinc, which was free, enters into combination, and the hydrogen, which was in combination, is set free; in other words, the zinc has been *substituted* for, or has *replaced*, the hydrogen.

It may here be stated that chemists of all nations have agreed to represent each of the elements by a symbol, which consists usually of

the first letter of the name of the element. Thus **O** is the symbol of oxygen, and **N** of nitrogen. If the names of two or more elements begin with the same letter, the initial letter is used, together with some other letter of the name. Thus **B** is the symbol of boron; **Bi**, of bismuth; **Ba**, of barium. **C** is the symbol of carbon; **Ca**, of calcium; **Cl**, of chlorine; **Cr**, of chromium. It is to be noted that these symbols have been derived from the Latin names of the elements, and that consequently there are some instances where the symbol has no resemblance to the English name of the element to which it refers. Thus the symbol of iron is **Fe**, from *ferrum*; that of potassium is **K**, from *kalium*; and that of mercury is **Hg**, from *hydrargyrum*. The symbol of copper is **Cu**, from *cuprum*.

These symbols serve not only as convenient abbreviations, but each stands for a *single atom* of the element indicated. If we know the atomic weight of the element, the symbol may stand to us also for a *certain definite weight* of the element in question, as we have seen in § 28. In § 29 the symbols **O** and **H** were used to indicate *one volume* of oxygen and hydrogen respectively. This use of the symbols to express volumetric relations is, however, not the same for all the elements, and it will be treated of in Chapter XI.

Two or more of the elementary symbols just described, when written together, stand for a molecule made up of the atoms indicated. Thus **HCl** stands for a molecule containing one atom of hydrogen and one atom of chlorine; **ZnCl₂** stands for a molecule made up of one atom of zinc and two atoms of chlorine; the figure 2 written *below the line* applies to the **Cl** alone. If the figure 2 were written *on the line*, and before the symbol, it would indicate two molecules of the compound, as **2HCl**. The knowledge of the atomic weights enables us to use the molecular symbols to express the composition of a substance by weight. Thus we have already seen (§ 28) that **H₂O** indicates that in every 18 parts by weight of water there are 16 parts by weight of oxygen, and 2 parts by weight of hydrogen. In the same way, knowing the atomic weight of chlorine to be 35.2, we perceive from the symbol **HCl** that in every 36.2 parts by weight of hydrochloric acid there are 35.2 parts by weight of chlorine, and 1 part by weight of hydrogen. We say the *molecular weight* of water is 18, and the molecular weight of hydrochloric acid is 36.2, meaning that the molecule of water weighs 18 times, and the molecule of hydrochloric acid 36.2 times, as much as the *atom of hydrogen*, which is taken as the unit of molecular as well as of atomic weight. The circumstances under which we may also learn the *volumetric* composition of a compound from the symbol of its molecule, will be discussed in § 171.

Symbols are constantly used by chemists for the purpose of recording briefly facts of observation, such as the results of experiments. By means of this short-hand it is easy to compress much informa-

tion into a very small space, for every well-understood chemical reaction may be written in the form of an equation. Thus, the equation just now given ($2\text{HCl} + \text{Zn} = \text{ZnCl}_2 + 2\text{H}$) sets forth the fact that, from the action of 2 molecules of hydrochloric acid and 1 atom of zinc upon each other, there result 1 molecule of zinc chloride and 2 atoms of hydrogen. Of course, as the experiment was actually performed, a vast number of molecules of hydrochloric acid, and the corresponding number of atoms of zinc, acted upon each other: the equation indicates merely the *relative* number. It follows naturally from the very conception of atoms and molecules, that, whenever chemical action takes place between two bodies, it is always between fixed and definite quantities of those two bodies. Our knowledge of the atomic weights of the various elements enables us to calculate from the equation what must be the relative proportion, by weight, of the substances concerned in the action. The atomic weight of zinc is 65, and the molecular weight of hydrochloric acid is 36.2; and from the equation we see, that, for every atom of zinc weighing 65 of our units of weight (the unit being the weight of an atom of hydrogen), 2 molecules of hydrochloric acid must be taken which weigh 72.4 (i.e., 2×36.2) of these same units. Moreover, from the action on each other, of these amounts of zinc and hydrochloric acid, there result 1 molecule of zinc chloride weighing 135.4 (i.e., $65 + 70.4$), and 2 atoms of hydrogen weighing 2 of these same units. It is, of course, immaterial whether the unit of weight be the weight of an atom of hydrogen, or a pound, or a kilogram: the relative proportion, according to which these two substances act upon each other, must be the same, and the following proportions will hold true in any case:—

Weight Zn in any case : weight HCl in same case = 65 : 72.4.

Weight Zn in any case : weight ZnCl_2 in same case = 65 : 135.4.

If the weight of zinc used in any case were given, the weight of hydrochloric acid required could be readily calculated, as we should then have three terms of a proportion given to find the fourth. Moreover, the amount of zinc chloride produced by the use of 65 parts of zinc would be $65 + (2 \times 35.2)$, that is, 135.4 parts by weight. In fact, if the amount of any one of the four substances were given, the amounts of the other three could be found, as they are all proportional (§ 87).

It is also to be remarked, that, in writing the equation, no account was taken of the water in which the HCl was dissolved. This water remained in the bottle unchanged after the experiment was finished, and in it the zinc chloride (ZnCl_2) formed was held in solution. It

would be possible, by the application of heat, to evaporate all of this water, and leave the zinc chloride as a solid substance.

As has been stated, every well-understood chemical reaction may be expressed in the form of an equation; for in a chemical process there is nothing lost,—there is no destruction of matter. There are, however, certain conditions which every equation must satisfy: it must represent an actual fact of observation; the weights represented on each side must be equal; and, what amounts to the same thing, the number of atoms of each element in the product must be the same as the number of atoms of the same kind in the factors. A chemical equation differs essentially from the algebraic expression called by this name, any inference that can be drawn from which must in some sense be true. Chemical equations are simply expressions of observed facts; and, although important inferences may often be drawn from them, these inferences are of little or no value until confirmed by experiment. Moreover, the facts expressed in this peculiar notation are as purely materials for memory as if they were expressed in common language.

39. Hydrogen occurs free in the gases of some volcanoes and natural-gas wells, in the atmosphere of the sun and of some fixed stars. It is an essential constituent of water and of all organized matter of animal or vegetable origin. It is a transparent, colorless, tasteless, and odorless gas. It is not poisonous, though animals die from suffocation when immersed in it, as they do in an atmosphere of nitrogen. It is exceedingly difficult to liquefy; but when subjected to very great pressure at an exceedingly low temperature it has been obtained in the form of a clear, colorless, transparent liquid. Gaseous hydrogen is exceedingly light, being about $14\frac{1}{2}$ times lighter than air, 11,160 times lighter than water, and 151,700 times lighter than quicksilver. A liter, under standard conditions of temperature and pressure, weighs 0.0896 g., which weight is called a *crith.* Hydrogen is the standard of specific gravity for gases, as water is for liquids and solids: its specific gravity is therefore unity. The term *vapor density* is usually applied to the specific gravity of a gas referred to hydrogen. The **vapor density** expresses how many times heavier a given volume of the gas is than the same volume of hydrogen under the same conditions of temperature and pressure.

40. The exceeding lightness of hydrogen can be illustrated

by filling soap bubbles with the gas. They will rise rapidly through the air; and, if touched with a lighted taper, the hydrogen will immediately burst into flame. Owing to its lightness, hydrogen can readily be poured or decanted upwards from one vessel to another.

Exp. 19. — Lift from the water pan a thick, strong, wide-mouthed bottle, of 200 to 300 cc. capacity, full of hydrogen, taking care to hold it in a perpendicular position, with the mouth downward. With the other hand place another bottle of equal size and strength, but containing only air, beside the hydrogen bottle, so that the mouths of the bottles shall touch at one edge. Gradually turn down the hydrogen bottle, and at the same time push its mouth beneath that of the air bottle in such manner that the bottle which originally contained the hydrogen shall at last stand upright beneath the inverted bottle. During this operation, the lighter hydrogen flows up into the upper bottle, while the heavier air sinks into the lower. If a burning match be now thrust into the upper bottle, the hydrogen within it will take fire; but, upon applying the match to the lower bottle, originally full of hydrogen, there will be found in it nothing but air.

Since hydrogen is thus lighter than air, it is not absolutely necessary, in collecting it, to operate over water, as has been directed. When a gas is much lighter or heavier than atmospheric air, it may often be conveniently collected by *displacement*. A bottle can be readily filled with hydrogen from a gas holder by carrying the delivery tube to the top of the inverted bottle, and allowing the gas to flow in. After a short time the air will be wholly displaced, and the bottle filled with hydrogen.

41. There is another noticeable peculiarity of hydrogen which is directly connected with its extreme lightness. It possesses in a high degree the power of *diffusion*. This diffusive power is a physical property common to all gases and vapors. In the case of hydrogen, it is only the intensity of the diffusive power which is remarkable. The following experiment will serve to illustrate this property:—

Exp. 20. — Into a small porcelain dish put two or three teaspoonfuls of plaster of Paris, together with rather less than half as much water. Mix the materials intimately, and close with the moistened plaster one end of a glass tube 3 or 4 cm. in diameter and 30 or 40 cm. long. The plug of plaster should be 1 or 2 cm. thick. Set the tube aside for a day or two, in order that the plaster may become dry. When the plug is dry, fill the tube with hydrogen by displace-

ment, and set it upright in a glass of water. Water will rise rapidly in the tube, since hydrogen escapes through the plaster more rapidly than air can enter the tube through this porous plug. If the tube be left to itself, air will slowly enter through the plaster, so that the water within the tube will in due time sink to the level of the outside liquid.



Fig. 10.

The velocities with which gases diffuse are inversely proportional to the square roots of their vapor densities: hence it happens that hydrogen, being the most attenuated of all gases, diffuses with the greatest rapidity. Compared with that of oxygen, its rate of diffusion is as 4 to 1; that is to say, the relative rates of diffusion of the two gases are inversely as the square roots of the numbers 1 and 16, which represent the vapor densities of hydrogen and oxygen respectively.

On account of its high diffusive power, hydrogen can be kept only in perfectly tight vessels. It cannot be kept for any length of time either in balloons or in bladders or rubber bags, and it will even leak through stopcocks which are sufficiently tight to retain nitrogen or oxygen.

42. Hydrogen is exceedingly inflammable, as has been already seen; that is to say, the temperature at which it takes fire is comparatively low. But, as a matter of course, it extinguishes any burning body which is immersed in it, since oxygen is necessary for the support of ordinary combustion.

Exp. 21. — Carefully lift from the water pan a bottle of 200 or 300 cc. capacity, completely full of hydrogen; slowly carry the bottle, the mouth of which is, of course, held downward, to a burning candle or splinter of wood, and depress the bottle over this flame. The hydrogen will take fire and burn below, at the mouth of the bottle, where it is in contact with the oxygen of the atmosphere; but the flame of the candle will be extinguished the moment it becomes completely enveloped by the hydrogen. The candle can easily be relighted by slowly lifting the bottle until the wick is brought into contact with the air and the burning hydrogen.



Fig. 11.

43. It has been seen that the hydrogen flame gives little *light*; it is, however, very *hot*. Indeed, it has been found that when a given weight of hydrogen enters into chemical union

with oxygen, more heat is developed than in the burning of the same weight of any other substance. A gram of hydrogen evolves by its combustion 34,180 cal. (§ 22); and from this fact is calculated the *heat of formation* of water, by which is meant the heat evolved when 2 g. of hydrogen unite with 16 g. of oxygen to form 18 g. of water. The heat of formation of water is then 68,360 cal. Similarly, in all cases of chemical combination a certain amount of heat is produced which can be expressed in terms of the thermal unit. On the great heat produced by the combustion of hydrogen depends the use of the so-called *oxyhydrogen blowpipe*.

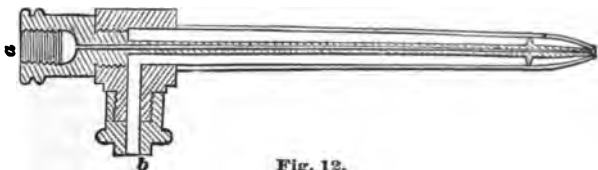


Fig. 12.

To burn hydrogen in oxygen requires special apparatus, the principle of the construction of which may be learned from Fig. 12. It consists essentially of two tubes, one within the other. The inner tube (*a*) is connected with a gas holder containing oxygen; the outer tube (*b*), with a gas holder containing hydrogen. The cock of the hydrogen gas holder is first opened, and the hydrogen is lighted at the point of the jet; the cock of the oxygen gas holder is then slowly opened until the flame is reduced to a fine pencil. A constant and sufficient pressure should be maintained on the gas holders.

In the flame thus produced, a fine platinum wire will readily melt, and fall down in drops. The intense heat of the oxyhydrogen flame is thus admirably illustrated, for platinum is an exceedingly infusible metal, which can scarcely be softened in the hottest furnace.

If a piece of chalk or lime, scraped to a fine point, be held in the flame of the oxyhydrogen blowpipe, it will quickly become white-hot, and evolve light of great brilliancy, almost comparable with that of the sun. On this principle is constructed the so-called *calcium light*, often employed for night signals and optical experiments.

44. No matter in what way hydrogen is burned, whether in the pure state or in combination with other materials, whether in pure oxygen or in the air, the *product* of the combustion is always *water*. At the high temperature of the flame, this

water must, of course, remain in the condition of a gas, but it can readily be brought to the liquid state by reducing the temperature.

Exp. 22. — Over a jet of burning hydrogen, best obtained from a gas holder, hold a dry, cold bottle. The glass soon becomes covered with a film of dew, as the water generated by the union of hydrogen and oxygen condenses in droplets upon the cold sides of the bottle.

45. If, instead of burning pure hydrogen as it flows into the air, the gas be first mixed with oxygen, and then ignited, a very different result will be obtained. The hydrogen being now in contact with oxygen at all points, the entire mass of gas will burn with a violent explosion at the instant when a light is touched to it.

This may be illustrated by connecting a piece of glass tubing with a gas holder, or, better, a rubber bag, containing a mixture of 2 volumes of hydrogen and 1 volume of oxygen. The end of the glass tube is dipped into a dish of soapsuds, and the gas allowed to flow until several bubbles of foam have formed on the surface of the suds. Care should be taken to avoid the formation of a large quantity of foam in this experiment, since the concussion is in any event deafening. If, after the removal of the gas holder, the foam be touched with a long lighted stick, a violent explosion will occur.

Any remnant of the mixture of hydrogen and oxygen which may have been left in the gas holder at the close of the experiment, should carefully be thrown away, and upon no account should fire ever be brought into its vicinity.

The loud explosion is owing to the fact that the intense heat emitted at the moment of the combination of the two gases expands enormously the steam formed by their union. As this steam is immediately condensed, and as the original mixture of the two gases occupied about 2,000 times as much space as the liquid water formed by their combination, there results a partial vacuum, into which air rushes from all sides; and it is the heavy and sudden undulations thus communicated to



Fig. 13.

the air which occasion the noise. The outward and inward shocks follow one another so quickly, that the ear cannot distinguish between them.

46. Mixtures of hydrogen and air produce less violent explosions than mixtures of hydrogen and oxygen, because of the inert nitrogen in the air, which acts as an elastic pad or cushion to break the force of the shock.

Exp. 23. — Introduce 2 volumes of hydrogen and 5 volumes of air into a strong round-bottomed bottle, such as is used for soda water. Close the mouth of the bottle with a cork, and shake violently, in order that the gases shall be mixed. A small quantity of water should be left in the bottle to act as a stirrer. Grasp the bottle firmly in one hand, remove the cork with the other, and apply the open mouth of the bottle to a lighted candle. An explosion will immediately ensue.

47. Since air is everywhere about us, and since all ordinary combustions occur in it, it has become customary to speak of it and of oxygen as *supporters of combustion*, in contradistinction to the so-called *combustibles*, such as hydrogen. These terms are often convenient; but that they have only a relative, and no absolute significance, may be shown experimentally as follows:—

Support a rather wide tube of thin glass—the neck of a broken retort, for example—in a vertical position, and connect the upper opening with a gas holder containing hydrogen. Allow the gas to flow until the tube is filled; then apply a lighted match to the mouth of the tube, and regulate the flow of gas so that the latter may continue to burn slowly at the lower edge of the tube.

With a second gas holder containing oxygen, connect a piece of narrow glass tubing drawn out to a fine point; and, while the oxygen is flowing through this tube, pass it up into the larger tube filled with hydrogen. As the stream of oxygen passes through the burning hydrogen at the bottom of the vertical tube, it takes fire, and afterwards continues to burn in the atmosphere of hydrogen within the tube. Care must be taken that no mixture of hydrogen and oxygen shall accidentally accumulate in the tube.

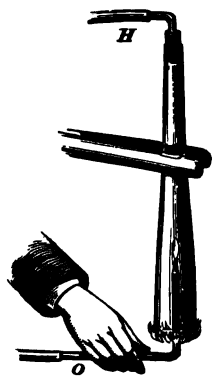


Fig. 14.

48. Hydrogen Dioxide. — Beside water, there is another compound of oxygen and hydrogen having the composition represented by the formula H_2O_2 . It is exceedingly unstable, readily giving off half its oxygen: thus it serves in the laboratory as a convenient oxidizing agent (§ 152). A weak aqueous solution, sometimes called *oxygenated water* or *peroxide of hydrogen*, is much used by surgeons and dentists as a germicide. One great merit of it, both in surgical and chemical operations, is, that when used, it leaves no residue other than pure water and the products of oxidation. The aqueous solution is also used for bleaching old prints and engravings, and for changing dark hair to lighter shades. Traces of hydrogen dioxide are to be found in the water of many showers of rain and snow; and the occasional sudden rusting of iron and steel objects, as seen in the case of railway tracks after certain showers, appears to be due to its presence.

CHAPTER VI.

COMPOUNDS OF NITROGEN.

49. We have already learned that nitrogen is, under ordinary conditions, a very inert substance, and indisposed to enter into chemical combination. There are, however, many compounds of nitrogen which either exist in nature, or may be prepared by indirect methods, and the study of the compounds of nitrogen and oxygen will bring clearly into view a fact of great significance. The study of water showed us that in a chemical compound the elementary constituents are combined in a certain *definite proportion*. The existence of another compound of hydrogen and oxygen, hydrogen dioxide, showed us that two chemical elements may combine in *more than one* definite proportion. A marked illustration of this fact is to be seen in a series of compounds of nitrogen and oxygen, five in number, which differ from each other and from the constituent elements.

50. Nitrogen Monoxide, or Nitrous Oxide (N_2O).— The first compound of nitrogen and oxygen which we shall study may be readily obtained by gently heating a substance known as *ammonium nitrate*, of which we shall learn more hereafter.

Exp. 24. — Into a *dry* flask of thin glass of about 300 cc. capacity introduce 10 or 15 g. of crystallized ammonium nitrate. From the flask placed upon the wire gauze on the iron stand, carry a delivery tube (No. 6) beneath the saucer in the water pan; but interrupt the tube at some convenient point to interpose, by means of a cork or caoutchouc stopper with two holes, a small bottle, which can be kept cool with water, as shown in the figure.

Heat the flask moderately and cautiously, to avoid breaking it.

The ammonium nitrate will melt, and little bubbles will soon begin to escape from the fused mass. The heat must now be so controlled that the evolution of the gas shall not be tumultuous. The gas is to be collected in bottles of 300 to 400 cc. capacity. If the process has been



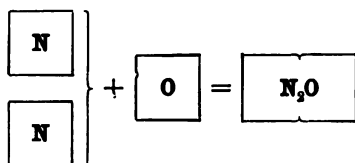
Fig. 15.

successfully conducted, there will be found in the cooled bottle through which the gas passes, a clear, colorless liquid, which, on examination, will prove to be water, and nothing else. If too high a temperature is employed, the liquid will have a slightly acid reaction. When two or three bottles of gas have been filled, and enough water for testing has condensed, the delivery tube may be withdrawn from the water, and the lamp extinguished. The ammonium nitrate might be entirely resolved into water and the gas which now awaits examination; but there is danger of breaking the flask. That the nitrate leaves no residue behind, when sufficiently heated, may be proved by heating a crystal of it on platinum foil over the gas lamp.

Exp. 25. — Insert a glowing splinter of wood into a bottle of the gas. It will re-inflame with almost as much energy as in oxygen. Or place a lighted candle in a bottle of the gas. It will burn more vigorously than in air.

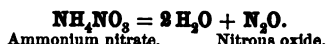
51. From the energy with which the glowing splinter bursts into flame, it may be inferred that oxygen is a constituent of the new gas which we have just prepared, and, indeed, repeated

experiments have shown that it is composed of the elements nitrogen and oxygen; and that, just as in the case of water two volumes of hydrogen and one volume of oxygen are condensed into two volumes of dry steam, so here two volumes of



nitrogen and one volume of oxygen are condensed into two volumes of this transparent gas. As the chemical formula or symbol of water is H_2O , so the formula of this new gas is

N_2O , and its volumetric composition may be represented by a diagram similar to that by which we conveyed to the eye the composition of water. The gas is called *nitrogen monoxide* or *nitrous oxide*. The equation which represents the chemical action by which it was produced may be thus written:—



From the above composition by volume, and from the known specific gravities of nitrogen and oxygen, the composition of nitrogen monoxide by weight is readily deduced. The specific gravity of nitrogen, referred to hydrogen, is 14; that of oxygen, 16. Since there are two volumes of nitrogen for each volume of oxygen, the two elements must, in any given weight of the gas, be combined in the proportion of 28 parts by weight of nitrogen to 16 of oxygen. The molecule of nitrogen monoxide (N_2O) must be composed, like any other quantity of the gas, of 28 parts by weight of nitrogen and 16 of oxygen; but, precisely as in the case of water, we conceive of the molecule as made up of two atoms of nitrogen and one atom of oxygen; and we have already learned, that, if the atomic weight of hydrogen be represented by 1, that of oxygen must be 16. It follows, from the constitution of nitrogen monoxide, that, if 16 represents the smallest proportional weight of oxygen which exists in combination, 14 must be the corresponding smallest weight of nitrogen when thus united with oxygen. Nitrogen monoxide contains $\frac{14}{16}$, or 36.36 per cent, of oxygen.

Exp. 26. — Place in a deflagrating spoon a bit of sulphur, and ignite it with the least possible application of heat. Thrust it at once into a bottle of the gas. It will be extinguished. Heat the sulphur much hotter, until it is burning actively, and again thrust it into the gas. It will now burn more brilliantly than in air. The burning of the sulphur and of the splinter in the nitrous oxide is at the expense of the oxygen it contains. Before the sulphur in this experiment can combine with oxygen, the nitrous oxide must first be decomposed. To accomplish this result, the sulphur must be hotter than it need be for simply burning in the air or in oxygen. In reality, two reactions are involved, — first, the decomposition of the nitrous oxide by heat; second, the combination of the sulphur with the oxygen set free. There are several gaseous compounds much richer in oxygen than either air or nitrous oxide, which cannot support ordinary combustion at all, simply because the common combustibles are unable to effect this decomposition and set free the oxygen.

52. Nitrous oxide is almost without odor, but has a distinctly sweet taste. Since it is somewhat soluble in water, there is a slight loss when collected as in the experiments. *When pure*, it may be respired for a few minutes with impunity. When inhaled, it produces a lively intoxication, attended with a disposition to muscular exertion and violent laughter; whence its trivial name of *laughing gas*. It may, however, be administered so as to cause complete insensibility to pain; the effect lasts, however, for only a very short time. It is advantageously used as an anæsthetic in such surgical operations as can be performed in a few seconds. When subjected to a temperature of 0° and a pressure of 30 atmospheres, it can readily be liquefied, and is now sold in a liquid state in wrought-iron vessels, for use as an anæsthetic in dental surgery.

53. Nitrogen Dioxide, or Nitric Oxide (NO or N_2O_2). — We now proceed to investigate another compound of nitrogen and oxygen which may be prepared from a chemical substance with which we shall soon be familiar, *nitric acid*.

Exp. 27. — Place 15 or 20 g. of copper turnings or filings in a bottle arranged as for generating hydrogen (Exp. 18, § 37), and pour upon them about 25 cc. of dilute nitric acid made by adding to the common strong acid its own bulk of water. Brisk action will immediately occur. The generator becomes filled with red fumes, which gradually disappear; and, when the gas disengaged is collected over

water, it is found to be colorless. Collect three bottles (of 300 to 400 cc. capacity) of this gas, adding acid from time to time, as may be necessary. Save the blue solution (copper nitrate) which remains in the generator for future use.



Fig. 16.

Exp. 28. — Dip a lighted candle into a bottle of the gas. The light is extinguished. Into the same bottle thrust a glowing splinter. It will not inflame.

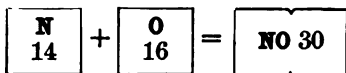
Exp. 29. — Lift a bottle of the gas from the water, so that air may enter the bottle, and the gas may escape into the air. Red fumes, of very disagreeable smell, and very irri-

tating when inhaled, are abundantly produced. Bring into contact with these fumes a piece of moistened litmus paper. It becomes red. The significance of this action will appear later.

Exp. 30. — *Thoroughly* ignite a bit of sulphur in a deflagrating spoon, and introduce it into a bottle of the gas. It will not burn. Into the same bottle thrust a piece of phosphorus as big as a pea, burning *actively*. The combustion will be continued with great brilliancy. It appears that in nitric oxide, though it contains a larger proportional amount of oxygen, the two elements are more firmly united than in nitrous oxide. Most burning substances are extinguished when immersed in it, a high temperature being required to set free the oxygen.

54. By the preceding experiments we learn that the new gas is transparent and colorless, and that it differs notably from all the other gases thus far studied in its relation to combustibles. Analysis shows that the gas consists of nitrogen and oxygen, one volume of each gas uniting to form two volumes of the compound gas. Its molecule will be represented by the formula NO ; and its elements are united by weight in the proportion of 14 parts of nitrogen to 16 of oxygen, because equal volumes of nitrogen and oxygen weigh respectively 14 and 16 times as much as the same volume of hydrogen. Its composition may be represented by the accompanying diagram. The gas is thus another oxide of nitrogen.

It is generally known as *nitric oxide*, though many chemists now regard the molecule as N_2O_2 , and name the compound *nitrogen dioxide*.



The action of the copper on the nitric acid in Exp. 27, § 53, may be represented by the following equation:—



55. When the same element forms more than one compound with oxygen, prefixes are often used to distinguish between them. The compound containing a single atom of oxygen in the molecule is called the *monoxide*; when the molecule contains two atoms of oxygen, the compound is called the *dioxide* or *binoxide*; and succeeding oxygen compounds would be the *trioxide* or *teroxide*, *tetroxide* or *quadroxide*, etc.; the relative proportions of oxygen contained in the molecule being indicated by the prefixes.

The term *peroxide* may be applied to any compound containing more oxygen than the simplest oxygen compound of the element to which the term *protoxide* is applied. If there are several oxides, it is often used conventionally to denote a particular one.

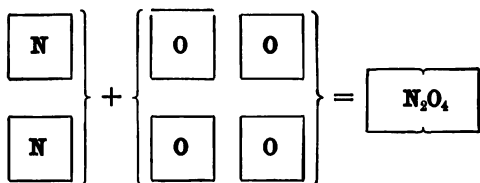
Sometimes the relative amount of oxygen is indicated by the terminations *ous* and *ic*. In this case, *ous* implies less oxygen than *ic*: nitrous oxide contains less oxygen than nitric oxide. These prefixes and terminations are not restricted, in their use, to oxygen compounds: we shall hereafter meet with such terms as *ferrous chloride* and *ferric chloride*, *cuprous iodide* and *cupric iodide*, etc.

56. **Nitrogen Trioxide (N_2O_3).** This oxide is formed when a mixture of nitric oxide with a large excess of oxygen is subjected to intense cold. It is contained in the gases given off when strong nitric acid and common starch are heated together.

Exp. 31.—Into a flask of about 250 cc. capacity put 50 cc. of strong nitric acid and 5 g. of starch. Warm the flask gently, and as

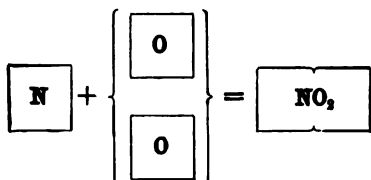
soon as the mixture begins to turn reddish brown, remove the lamp. The experiment should be performed where there is a good draught of air, as the red fumes are copiously evolved when the action once begins. Nitrogen trioxide condenses easily to a liquid of a blue color, stable only at a low temperature. This compound is sometimes called *nitrous anhydride* (§ 71). The blue liquid is so unstable that it is not easy to study its composition or its qualities; but it may be regarded as consisting of an oxide of nitrogen differing decidedly from those heretofore studied, — an oxide capable of direct derivation from nitric oxide by adding to any volume of this last one fourth that volume of pure oxygen; whence it follows that its formula should be written N_2O_3 , and that it is composed of 28 parts by weight of nitrogen, and 48 parts by weight of oxygen. Nitrogen trioxide mixed with a little cold water probably forms nitrous acid ($N_2O_3 + H_2O = 2HNO_2$). The acid itself is not known in a free state, though many saline substances formed from it by the replacement of the atom of hydrogen by other elements exist, and several of them are frequently put to use in laboratories. These saline compounds are called *nitrites*.

57. **Nitrogen Tetroxide, or Nitrogen Peroxide (N_2O_4).**—The red fumes of Exp. 29, seen when nitric oxide was brought into contact with the air, were due to the chemical union of nitric oxide with oxygen. A fourth oxide of nitrogen was formed, — *nitrogen peroxide*. The molecule of this substance will be represented by the formula N_2O_4 , and its composition by weight will be 28 parts of nitrogen and 64 of oxygen in every 92 parts by weight of nitrogen tetroxide.



Taken in the condition in which it exists at low temperatures, the volumetric composition of gaseous nitrogen tetroxide may be represented by the diagram above given; but, on heating the gas to a temperature of 140° , the more complex molecules of N_2O_4 are broken up, and entirely resolved into simpler molecules of NO_2 . Hence, at the higher temperature,

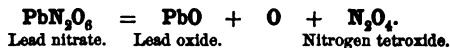
the volumetric composition of the gas may be represented by the following diagram:—



By some chemists the term *nitrogen peroxide* is restricted to the gas in the latter form, NO_2 , and the name *nitrogen tetroxide* is used to designate the gas when the molecules have the composition represented by N_2O_4 .

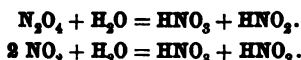
58. Although at ordinary temperatures nitrogen tetroxide is a gas, it can readily be condensed to a liquid. To this end it may be prepared by heating a substance known as *lead nitrate*.

Exp. 32.—Fill a perfectly dry ignition tube about one third full of lead nitrate which has been finely powdered and *thoroughly dried*. Connect the ignition tube with a dry bottle, and finally with the water pan. The arrangement is similar to that in Fig. 15, except that the flask is replaced by an ignition tube. The small bottle must be surrounded by a mixture of ice (or snow) and salt. Heat the ignition tube gently; and, when the evolution of gas has once begun, care must be taken that the tube is not suffered to cool, so as to allow the water to suck back from the water pan. Red fumes will fill the delivery tubes, and will condense in the small bottle to a brownish yellow liquid, if the experiment is successful. A colorless gas will collect at the water pan. It is oxygen, as may be shown by the insertion of a glowing splinter. The chemical action may be thus represented:—



The experiment just performed is interesting, as showing the transformation of a substance which is usually a gas, into a liquid: in this case it was only necessary to lower the temperature. Many other gases may be liquefied in the same manner by being cooled to a low temperature; and, by the application of a very great pressure at the same time, it has been found possible to liquefy all known gases, excepting hydrogen, although several of them had long been regarded as permanent

or incondensable. Nitrogen tetroxide reacts with water to form nitrous and nitric acids, —



59. **Nitrogen Pentoxide, or Nitric Anhydride (N_2O_5).**—A fifth oxide of nitrogen is an unstable, white, solid compound whose symbol is N_2O_5 . It is called *nitric anhydride*, and is closely related to nitric acid. Nitric acid we have already used, and have learned that its symbol is HNO_3 . If the oxide N_2O_5 be treated with water, the action which takes place may be represented by the equation —



which expresses the fact, that, by the union of one molecule of water and one molecule of nitric anhydride, there are formed two molecules of nitric acid. On account of this reaction, nitric acid may be, and is sometimes, regarded as a *compound* of nitric anhydride and water; and its formula may be written, $\text{H}_2\text{O} \cdot \text{N}_2\text{O}_5$. The origin and propriety of the term *nitric anhydride* now becomes apparent: for this oxide of nitrogen, although it is obtained directly from nitric acid only with difficulty, may evidently be regarded as nitric acid deprived of water; that is, rendered *anhydrous*.

60. The relative proportions of oxygen and nitrogen have been determined by weight in the case of the oxides N_2O , and N_2O_3 , but not by volume, as was done with all the other oxides of nitrogen. The reason for this is that they cannot be converted into gases without undergoing decomposition. By indirect methods, however, their volumetric composition has been determined.

61. The oxides of nitrogen, then, are —

| Name. | Symbol. |
|---------------------------------------|--|
| Nitrogen monoxide (protoxide) | N_2O |
| Nitrogen dioxide (nitric oxide) | N_2O_3 |
| Nitrogen trioxide (nitrous anhydride) | N_2O_5 (from which we get nitrous acid, HNO_2) |
| Nitrogen tetroxide (peroxide) | N_2O_4 |
| Nitrogen pentoxide (nitric anhydride) | N_2O_5 (from which we get nitric acid, HNO_3) |

62. These five bodies are all *chemical compounds*. They are definite and constant in composition; and all differ essentially from their elementary constituents and from each other, as the experiments we have performed with several of them have demonstrated. It is therefore obvious that two of the elements are capable of combining in several proportions to form definite chemical compounds; and what is here proved of two of the elements we shall hereafter find to be true of all, although not of every couple: so that the series of oxides of nitrogen is but one illustration of a most comprehensive law. The difference between a mechanical mixture and a chemical compound does not on this account become less marked. The possible *mixtures* of nitrogen with oxygen are innumerable. The known *combinations* of these two elements are only five: two volumes of nitrogen combining chemically with either one, two, three, four, or five volumes of oxygen, and with no other proportions whatsoever. As for volumes, so for weights: the proportional weight of oxygen in these oxides rises by definite leaps from the first member of the series to the last.

This definite, step-by-step mode of forming chemical compounds is one of the most characteristic, as it is one of the most general, facts of chemistry: it is the habitual mode in which the force called *chemical* ordinarily acts. The abstract results of observation and experiment may be expressed in the following proposition, often called the **Law of Multiple Proportions**: *If two bodies combine in more than one proportion, the ratios in which they combine in the second, third, and subsequent compounds, are definite multiples of those in which they combine to form the first.*

The series of compounds of oxygen and nitrogen exemplify the law very clearly, as is seen in the following table, representing the quantities of oxygen which combine with a definite weight of nitrogen in each instance:—

| | N | O |
|---|----|---------------|
| Nitrogen monoxide (N_2O) | 28 | 16 |
| Nitrogen dioxide (N_2O_2) | 28 | 16×2 |
| Nitrogen trioxide (N_2O_3) | 28 | 16×3 |
| Nitrogen tetroxide (N_2O_4) | 28 | 16×4 |
| Nitrogen pentoxide (N_2O_5) | 28 | 16×5 |

63. Air a Mixture. — The distinction between a mechanical mixture and a chemical combination may be illustrated by the differences between common air and the oxides of nitrogen. Some of the considerations which go to show that air is simply a mechanical mixture of oxygen and nitrogen are as follows: —

In the first place, while in the oxides of nitrogen the two elementary gases bear to each other some simple relation in respect to both volume and weight, in air they are mixed in the far from simple proportion of 20.96 volumes of oxygen to 79.04 volumes of nitrogen, or 23.18 parts by weight of oxygen to 76.82 parts of nitrogen. Moreover, if 23.18 parts of oxygen are mixed with 76.82 of nitrogen, there is no development either of light, or heat, or electricity, such as usually attends the formation of a chemical compound; and the physical characteristics of the mixture are such as should, according to calculation, belong to a mere mixture of the gases.

Again, if nitric oxide be brought into contact with air, suffocating red fumes of nitrogen tetroxide are formed; but, if the nitric oxide be brought into contact with nitrogen monoxide, no fumes are produced, although this gas contains as much oxygen as common air. These experiments go to show, that, while in nitrogen monoxide the oxygen is held in chemical combination, in air it is free.

Further evidence that air is a mere mixture is afforded by its behavior towards water. All gases are soluble in water to a greater or less extent, each one dissolving in a certain fixed and definite proportion at any given temperature. If pure water be exposed to nitrogen monoxide, it will dissolve a certain amount of that gas, which may be recovered unchanged by boiling the water. When water which has been exposed to the air is boiled, a gaseous mixture containing oxygen and nitrogen is given off (Exp. 11, § 35); but it has been found that the gases are mixed in a different proportion from that in which they exist in the atmosphere. The water, in fact, dissolves out from the air a quantity of oxygen, just as if no nitrogen were present; at the same time it dissolves nitrogen to precisely the same extent that it would dissolve that gas if there were

no oxygen in the air. Again, the composition of a chemical compound is invariably the same. In all cases where chemical combination takes place, it is found that the elements combine in exactly the same proportions by weight to form the same products. But the composition of air varies slightly, according as it is taken from upper or lower layers of the atmosphere.

64. Nitric Acid (HNO_3).—In the preparation of the various oxides of nitrogen, we have used either nitric acid or a compound which we have designated as a *nitrate*; as, for example, ammonium nitrate in Exp. 24, § 50, and lead nitrate in Exp. 32, § 58. We now proceed to a study of those compounds, and, in the first place, of *nitric acid* itself. Two abundant sources of this material are found in nature, and are familiar as articles of commerce. Saltpeter or niter, a whitish saline crystallized substance, now mainly brought from India, is one of these sources. A similar substance, known in commerce as *nitrate of soda*, is collected on a desert tract in Chile, and forms a valuable article of export from that country. These two substances differ from each other only in this,—that the first contains potassium, the second the very similar element sodium, in either case combined with definite proportions of the elements nitrogen and oxygen. By the reaction of sulphuric acid (oil of vitriol) on either of these two substances, nitric acid is obtained.

Exp. 33.—Into a tubulated glass-stoppered retort of 250 cc. capacity put 40 g. of powdered potassium nitrate, or, better, 34 g. of powdered sodium nitrate, if it can be obtained; and through the tubulure pour 50 g. of strong sulphuric acid (H_2SO_4) which has been weighed out in a bottle previously counterpoised upon the balance with shot or coarse sand. Embed the bottom of the retort in sand contained in a small iron pan placed over the gas lamp on a ring of the iron stand. Thrust the neck of the retort into a receiver with two tubulures. The retort neck should fit the tubulure of the receiver with tolerable accuracy. The second tubulure of the receiver should be left open, or loosely covered with a bit of glass, in order to avoid the possibility of any pressure being created within the retort during the operation. Place the receiver in a pan of cold water, and cover it with cloth or soft paper, which must be kept wet during the distillation (Fig. 17). Heat the sand bath *moderately* (that the frothing which

occurs may not become too violent). Reddish vapors appear for a moment, then disappear, and a yellowish fuming liquid begins to condense in the neck of the retort and to run down into the receiver.

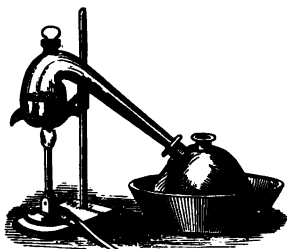


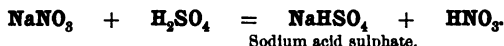
Fig. 17.

When all frothing has ceased and the mass in the retort is in a state of tranquil fusion, while very little liquid passes over into the receiver, the lamp is to be put out.

The very acid, corrosive, and poisonous liquid in the receiver is nitric acid. Its faint color is not its own, but is due to the presence of a compound of nitrogen and oxygen already described (N_2O_4). Transfer the liquid to a glass-stoppered bottle, and keep it for future use. In

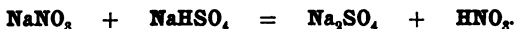
all manipulations with nitric acid it is desirable to avoid getting it upon the skin, since it produces rather permanent yellow stains.

As the retort cools, the residue solidifies into a white saline mass, which may be dissolved out of the vessel by repeated additions of warm water after the apparatus has become thoroughly cold; care being taken not to shake the hard cake, lest the thin glass of the retort be broken. It will be observed that the liquid sulphuric acid has disappeared, although the saline residue is still intensely acid. When sodium nitrate is treated with sulphuric acid, the action taking place is represented by the equation —



Sodium acid sulphate.

If sufficient sodium nitrate is present, and the temperature is quite high, a second reaction takes place, by which the normal sodium sulphate is formed, —



Normal sodium sulphate.

At the temperature required to bring about the latter reaction, much of the acid is decomposed into nitrogen tetroxide, water, and oxygen. 2HNO_3 heated $= 2\text{NO}_2 + \text{H}_2\text{O} + \text{O}$. The same change occurs slowly when the strong acid is exposed to sunlight.

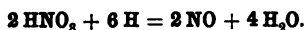
65. Nitric acid is much used in the arts, and is prepared on the large scale from the same materials as here employed. The retorts are large iron cylinders or kettles, and the acid is collected in stoneware receivers. The residue remaining in the retorts is a mixture of sodium sulphate and sodium acid sulphate known as *niter cake*.

A weaker commercial acid known as *aqua fortis* contains from 30 to 70 per cent of strong nitric acid. *Fuming nitric acid* is the strong acid containing a considerable quantity of nitrogen tetroxide. The pure acid is colorless, and is about half as heavy again as water. It may be mixed with water in all proportions.

Exp. 34. — To about 1 cc. of the nitric acid obtained in the last experiment add 10 times its bulk of water. Notice the sour taste by touching a drop of this diluted acid to the tip of the tongue. Into the solution thrust a strip of litmus paper: it will be turned red, showing that in spite of the amount of water added, the liquid is still strongly acid. Litmus is a blue coloring matter, prepared from various lichens. Unsized paper, colored with a solution of litmus in water, is a convenient test for many acids, which, as a rule, change the color of the paper from blue to red.

66. A very characteristic property of nitric acid is that of staining the skin yellow. It produces a similar effect upon most animal and vegetable matters, especially if they contain nitrogen. When sulphuric or hydrochloric acid is spilt upon the clothes, a red stain is usually produced, and a little ammonia water (§ 77) may restore the color; but nitric acid produces yellow stains, and ammonia merely intensifies the color instead of removing it, though it may prevent the acid from decomposing the cloth. The facility with which nitric acid, especially when hot, parts with its oxygen, renders it a valuable oxidizing agent. Few substances capable of forming compounds with oxygen escape oxidation when treated with it. When nitric acid is brought into contact with metals, it often happens that the metal takes the place of the hydrogen of the acid; but instead of this hydrogen being given off, as in the action between zinc and hydrochloric acid (Exp. 18, § 37), nitric oxide (N_2O) is obtained, as was seen in the preparation of this oxide of nitrogen by treating copper with nitric acid.

Exp. 35. — In each of two test tubes place a few bits of granulated zinc. To the one add a little dilute hydrochloric acid; to the other, an equal amount of strong nitric acid diluted with an equal volume of water; and warm the tubes gently. In the first case, hydrogen will be set free; while the action of the nitric acid will result in the copious evolution of red-brown fumes from the combination of the oxide of nitrogen set free with oxygen of the air.



This action of nitric acid finds its explanation in the fact that the hydrogen replaced by the metal is at once acted upon by a part of the

acid, with formation of nitric oxide and water. Other compounds of oxygen and nitrogen may be formed in this reaction, according to circumstances; and under certain conditions a part of the hydrogen may unite with nitrogen, and some ammonium nitrate be produced.

67. Acids, Bases, and Salts.—Nitric acid is an example of the class of bodies to which the term *acid* is generally applied. There is another class of bodies which act upon vegetable colors in just the opposite way from the acids, and will in fact *neutralize* their action in many cases. As an example of these substances, which are generally spoken of as *bases*, and which when soluble in water have what is called an *alkaline* reaction, we may take caustic potash, chemically known as *potassium hydroxide*.

Exp. 36.—Dissolve about 1 g. of caustic potash in 20 cc. of water. Notice the character of the solution by rubbing a little between the fingers, and by touching a small drop to the tip of the tongue. Into the liquid thrust the litmus paper which was reddened by the nitric acid in Exp. 34, § 65: it will be turned blue.

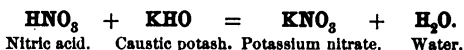
The terms *acid* and *base* cannot be defined with exactness. It has so long been customary to use both these terms broadly and loosely, that it is now impracticable to restrict the meaning narrowly. It may be said in general terms, that acids have a sour taste, and act in a peculiar way upon certain vegetable coloring matters; while bases, as has just been said, are not sour, and do not act like acids on these coloring matters. Moreover, bases, when they are soluble in water, exhibit alkaline properties which are distinctly different from those exhibited by acids.

An important characteristic of acids and bases is that they have the power, when one of either class reacts upon one of the other and opposite class, of forming new substances possessing the characters of neither the acid nor the base from which the new compound or *salt*, as it is called, has been formed. Certain elements in uniting with hydrogen and oxygen commonly form acids, while other elements form bases. The so-called *nonmetallic elements*, such as nitrogen, sulphur, etc., generally form acids; for example, nitric acid (HNO_3) and sulphuric acid (H_2SO_4). The *metallic elements*, such as potassium, sodium, copper, etc., form bases. Thus potassium hydroxide (KHO), sodium hydroxide (NaHO), copper hydroxide $\text{Cu}(\text{HO})_2$, are bases.

68. The relations between acids and bases may be illustrated by the following experiment:—

Exp. 37.—To one third of the nitric acid of Exp. 33, § 64, diluted with twice its bulk of water, add cautiously a rather dilute solution of

caustic potash (potassium hydroxide, KHO) until the mixture turns litmus paper neither red nor blue. Evaporate the solution in a porcelain dish, taking care that the liquid does not actually boil, until a drop taken out on the end of a glass rod becomes nearly solid on cooling. Then remove the lamp, and allow the dish to become cold. The crystals which will separate from the liquid are potassium nitrate, a compound which has already been used in the manufacture of nitric acid. The change that has taken place may be thus symbolized:—



The water in which the nitric acid and caustic potash were dissolved, together with that set free by the reaction, has for the most part been removed by evaporation. It might have been removed entirely if the evaporation had been carried further. The potassium nitrate would then be obtained as a white crystalline substance, but not in well-defined crystals.

When, as in the above experiment, an acid and a base react upon each other, there is formed, beside water, a new compound. This compound is called a *salt*, the name being applied to it on account of the general resemblance which this class of compounds bear to common salt, — one of the earliest known and most familiar of saline bodies.

69. If we compare the formula of nitric acid (HNO_3) with that of potassium nitrate (KNO_3), we shall observe a striking resemblance between the two. The two formulas are, in fact, identical, except that in the one case we have K (the symbol for potassium), where in the other we have H (the symbol for hydrogen). Potassium nitrate is only one of a class of analogous compounds called *nitrates*. The formula of each member of the class is that of one or more molecules of nitric acid (HNO_3 , $\text{H}_2\text{N}_2\text{O}_6$, etc.), except that the hydrogen is replaced by some metallic element. We have, indeed, already used several of these nitrates. Thus in Exp. 32, § 58, we used lead nitrate, the symbol of which is PbN_2O_6 ; and in Exp. 27, § 53, we prepared copper nitrate which remained in the solution, and the symbol of which is CuN_2O_6 .

In general, the salt may be regarded as derived from the acid by the replacement of hydrogen by a metallic element. Indeed, the essential

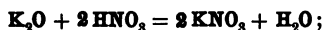
characteristic of the true acids is that they contain one or more atoms of hydrogen that can thus be replaced by base-forming atoms, or by groups of atoms acting as single atoms. No sharp line can, however, be drawn between acids and bases, and the conditions under which reactions take place in many cases determine whether the compound of an element with hydrogen and oxygen shall act as an acid or as a base. We shall have several examples of hydroxides, which, while they usually play a basic part, are capable of acting as acids.

70. Acids are classified according to the number of hydrogen atoms in the molecule that can be replaced by a metallic element. Those with one atom replaceable are termed *monobasic*; with two atoms, *dibasic*; with three atoms, *tribasic*; etc. To determine the class to which an acid belongs, we may find out by experiment how many salts can be derived from it by replacing its hydrogen with such a metal as potassium, the atom of which, as seen from the composition of the nitrate, is capable of taking the place of a single atom of hydrogen. It is quite evident that we can have only one potassium salt with a monobasic acid; but in a dibasic acid we have two atoms of hydrogen which may be replaced, H_2SO_4 , giving KHSO_4 and K_2SO_4 . In tribasic acids we have, similarly, the possibility of three salts, according as one, two, or three hydrogen atoms are replaced by atoms of potassium or some other metal. Salts are classified as *normal salts*, *acid salts*, and *basic salts*. When all the replaceable hydrogen of an acid has been replaced by a metal, we get a normal salt, as Na_2SO_4 (normal sodium sulphate); but, when only a part of the hydrogen is thus replaced, an acid salt results, as NaHSO_4 (sodium acid sulphate, a compound which still contains some of the characteristic hydrogen of the acid). Basic salts are salts formed from the acid by the replacement of the hydrogen, not by the metallic element alone, but by the metallic element combined with oxygen, or with oxygen and hydrogen; the compound still containing some of the oxygen, or oxygen and hydrogen, of the base. For example: bismuth hydroxide (BiH_3O_3) is a base; the normal nitrate of bismuth is $\text{Bi}(\text{NO}_3)_3$; but there is a basic nitrate of bismuth of the composition BiONO_3 , and this compound still contains some of the characteristic elements of the base, in addition to the metallic atom.

Many writers have sought to restrict the terms *acid* and *base* to the so-called *hydroxides*, — i.e., to compounds of hydrogen, oxygen, and some one other element; as, for example, nitric acid (HNO_3), and for a base potassium hydroxide (KHO), — and to apply the term *salt* to compounds formed by the reactions of these acid and basic hydroxides. But this proposed “rule” has never been generally accepted, and the term *acid* continues to be applied to many compounds which contain no oxygen, such as hydrochloric acid (HCl), and the other acids formed by the union of hydrogen with a member of the halogen group (§ 117); while the term *salt* is still habitually used in speaking of sodium chloride and analogous compounds. Salts corresponding to these hydrogen acids are properly known as *halides*, and are designated by words ending in *ide*: thus *fluorides*, *chlorides*, and *bromides* correspond to *hydrofluoric*, *hydrochloric*, and *hydrobromic* acids respectively.

As the *nitrates* correspond to *nitric acid*, so, corresponding to every acid, there is a series of salts, the name common to all the series being derived from the name of the acid. Thus, corresponding to *sulphuric acid*, there are numerous *sulphates*; corresponding to *phosphoric acid*, there are *phosphates*; to *oxalic acid*, *oxalates*; etc. As will be noticed in the cases above mentioned, the acid is designated by a term ending in *ic*, and the term applied to the salts ends in *ate*. If, however, the name given to the acid ends in *ous*, the name given to the salts ends in *ite*: thus, corresponding to *nitrous acid*, we have a series of *nitrites*; thus, nitrous acid (HNO_2), potassium nitrite (KNO_2).

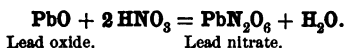
71. **Further Use of the Terms Acid and Base.** — Moreover, the term *base* is often used to denote compounds which contain no hydrogen. If potassium oxide (K_2O), which may be formed by heating metallic potassium in dry air or in oxygen gas, be treated with nitric acid, the following reaction will take place: —



and the same salt, potassium nitrate (KNO_3), is produced as was obtained in Exp. 37, § 68, where potassium hydroxide and nitric acid were brought together. On account of their taking part in such reactions as these, the anhydrous or basic oxides of the

metallic elements are often spoken of as bases. In some instances, indeed, the oxide is more commonly employed than the hydroxide in neutralizing acids and in forming salts. This is the case with oxide of lead.

Exp. 38. — Put 5 cc. of the nitric acid which remains from Exp. 33, § 64, into an evaporating dish, and dilute it with twice its bulk of water; then add 5 g. of finely powdered litharge (PbO), warm the mixture, and filter the liquid while hot into another evaporating dish. Evaporate the solution carefully to dryness, using a very gentle heat. There remains a white saline substance, which is lead nitrate, such as was used in Exp. 32, § 58. Its formation is thus represented: —



The term *anhydride* (or, more definitely, *acid anhydride*) is commonly applied to an oxide of a nonmetallic element, which, in combination with the elements of water, forms an acid, as was illustrated by nitric anhydride in § 59. To these anhydrides the term *acid* was formerly applied, as well as to the acids proper. To distinguish between the two sorts of compounds, the terms *anhydrous* and *hydrated* were employed: thus N_2O_5 was known as anhydrous nitric acid; and HNO_3 , as hydrated nitric acid.

NITROGEN AND HYDROGEN.

72. Nitrogen and Hydrogen. — There are three well-defined compounds of nitrogen and hydrogen, — ammonia (NH_3), diamid or hydrazin (N_2H_4), and hydrazoic acid or azoimid (N_3H). The first of these substances is much the most important. It is a gas, and may readily be prepared from ammonia water, — the *aqua ammoniæ* of the druggists.

Fill a flask of 250 to 500 cc. capacity about half full of the strongest ammonia water to be had at the druggist's. Close the flask by a cork provided with a funnel tube and an exit tube; carry the delivery tube to the bottom of a tall bottle, having a capacity of at least a liter, and filled with fragments of quicklime. When the ammonia water in the flask is gently boiled, the gas which passes off will be deprived of moisture by the quicklime, and will issue dry from the

bottle. It may be collected by upward displacement, as shown at the upper right-hand corner of Fig. 18; or it may be collected over mercury, as shown at the lower part of the figure. The gas is so extremely soluble in water, that it cannot be collected over the ordinary waterpan. As it has little more than half the density of atmospheric air, it can readily be collected by upward displacement. When thus collected, the gas should be allowed to pass into the *very loosely* corked bottle, until a piece of turmeric paper, held at the mouth, is immediately turned brown, or red litmus paper turned blue; the delivery tube is then withdrawn, and the mouth of the bottle is tightly closed with a caoutchouc or cork stopper.

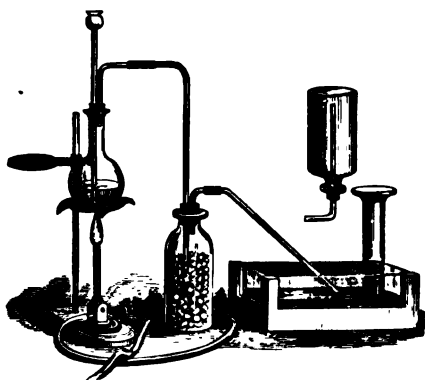


Fig. 18.

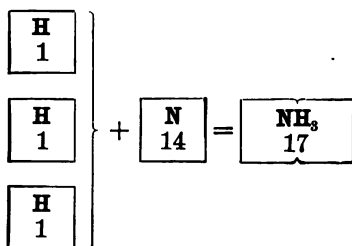
If the gas be collected over mercury, the flask must be provided with a very long funnel tube: for the pressure to be overcome by the gas, in forcing its way through even a few centimeters of mercury, is quite considerable; and, unless the funnel tube were long enough to sustain a column of liquid exerting an equal pressure, the liquid in the flask would be forced out through this tube. Great care must be taken to avoid inhaling the gas in any quantity.

The gas thus obtained is transparent and colorless, possesses an extraordinarily pungent odor which provokes tears, and has an acrid, alkaline taste. It will be found to be un inflammable, and not a supporter of ordinary combustion; it is, of course, irrespirable. It turns red litmus to blue most energetically. One volume of water at 0° dissolves 1,049 volumes of the gas.

The ready solubility of ammonia gas may be illustrated as follows: Fill a stout glass tube—an ignition tube, for example—by upward displacement, or over mercury, with the gas; grasp the tube by the top, and, holding it upright, dip its mouth into a vessel of water colored red with a little litmus. The water will rush up the tube, if the gas be pure, with a force which might break the tube if too thin.

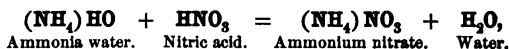
73. The solution of ammonia, if exposed to the air, or placed in a vacuum, or simply boiled, loses all its gas. When the gas is cooled to 0° and subjected to a pressure of $4\frac{1}{2}$ atmospheres, it is converted into a transparent mobile liquid. The gas may also be liquefied at the ordinary pressure if cooled to -40° , and be solidified at -75° . Liquid ammonia, in passing into the gaseous state, absorbs a large amount of heat from surrounding objects. In certain machines for the production of ice artificially, advantage is taken of this fact, the necessary cooling of the water being produced by the rapid evaporation of liquefied ammonia gas in contact with the vessel containing the water.

74. Analysis of dry ammonia gas has shown that it is made up of nitrogen and hydrogen in the proportion of one volume of nitrogen to three volumes of hydrogen, the four volumes of the elementary gases being condensed to two volumes in the compound. The formula of its molecule is NH_3 , and its composition may be represented by the diagram —

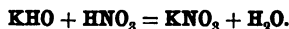


75. **Ammonium Salts.** — Since ammonia water gives off the gas so easily when boiled, or even when exposed to the air, it might seem, at first sight, that it was a case of simple physical solution; there is, however, good reason for considering that each molecule of ammonia is in combination with a molecule of water, in the form of the compound NH_4HO or NH_4O . This compound may be supposed to be dissolved in the water present in excess of what is necessary to form the compound. A considerable rise of temperature occurs when the gas is passed into water, owing partly to the liquefaction of the gas, and

partly, no doubt, to its chemical combination with the water. When ammonia water is mixed with nitric acid, a reaction occurs like that which takes place when nitric acid is mixed with a solution of potassium hydroxide (Exp. 37, § 68): there is formed a salt, called *ammonium nitrate*, resembling potassium nitrate; but, in order to bring out the resemblance, the elements of the compound of ammonia and water must be so arranged as to exhibit its analogy with potassium hydroxide, the formula of which is **KHO**. For that purpose, its formula must be written **NH₄HO**, so that the group of elements **NH₄** shall stand in the formula of ammonia water where the element potassium stands in the formula of potassium hydroxide. The reaction between ammonia water and nitric acid may then be represented by the equation —



just like —



If, now, the formula of ammonium nitrate, **(NH₄)NO₃**, be compared with that of nitric acid (**HNO₃**), it will appear that the group of atoms **NH₄** replaces the atom **H**, just as the atom **K** did in the formula of potassium nitrate. For this reason it has been found convenient to give to this group of atoms a name bearing some resemblance to the names of metals, and it has been called *ammonium*. A group of atoms such as this, acting together like a single atom, is called a *compound radical*. Ammonium is known only in its compounds. Many attempts have been made to obtain it in a free state, but hitherto in vain. As soon as the group of atoms escapes from combination, it is resolved into ammonia and hydrogen. The important compounds into which ammonium enters, commonly called the *salts of ammonium*, will be studied hereafter in immediate connection with the analogous salts of sodium and potassium.

76. Ammonia occurs in very minute quantity in the atmosphere, and hence in rain water, fog, and dew. It is given off by putrefying animal and vegetable substances containing

nitrogen, and almost every process of slow oxidation in the presence of air and moisture is attended with the formation of ammonia or ammonium salts. The chief source, however, of ammonium compounds is the decomposition, either by putrefaction or by destructive distillation, of nitrogenous organic matter. The distillation of bones, for example, for the purpose of making boneblack, yields a considerable amount of ammoniacal liquor, which was formerly the principal source of ammonium compounds. The horns of deer used to be thus distilled, whence the name *spirits of hartshorn*. At present the destructive distillation of coal in gas works furnishes the great bulk of the ammonium compounds used in the arts.

77. The solution of ammonia gas in water is a reagent continually required as a test in the laboratory, and is much used in the arts. The solution is colorless, intensely alkaline, has a caustic taste, and, when concentrated, blisters the skin. It is lighter than water, and so much the lighter in proportion to the amount of ammonia it contains. The solution may be prepared from a mixture of ammonium chloride and slaked lime.

Exp. 39.— Mix 25 g. of ammonium chloride, a substance generally sold under the name of *sal ammoniac*, with about the same weight

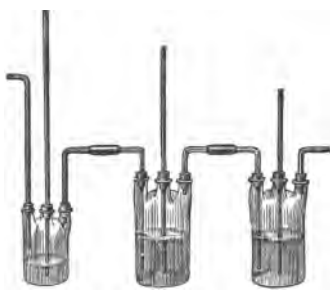


Fig. 19.

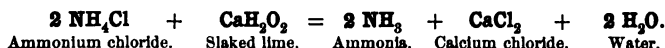
of cold, freshly slaked lime. Introduce the mixture into a flask of 500 cc. capacity, and place the flask on a sand bath over the gas lamp. Close the mouth of the flask with a good cork, provided with a delivery tube so bent as to connect conveniently, by means of a caoutchouc connector, with the first of the series of three-necked bottles (Woulfe bottles) represented in Fig. 19. On heating the mixture, ammonia gas will be disen-

gaged, and will be absorbed by the water in the Woulfe bottles.

The first of this series of bottles is smaller than the rest, and is not filled so full of water as the others: it should be kept cool by immersion in cold water. The delivery tube coming from the flask into this bottle must *not* dip into the water at all; so that it will be impossible for any water to suck back into the flask, should the gas suddenly cease to come off from the dry mixture. The construction of

the apparatus will be easily understood from the figure. The open tube which dips beneath the water in each bottle is a safety tube, which, by admitting air into any bottle in which a partial vacuum may happen to be created by rapid absorption, prevents the contents of the succeeding bottle from flowing back into it. In order to show the action of the safety tubes, the open tube in the first bottle may be closed for a moment with the finger, while the ammonia gas is passing into it, and the bottle shaken very gently. Water will be immediately forced back from the second bottle through the connecting tube to fill the vacuum caused by the absorption of the ammonia; but, the moment the finger is removed from the safety tube, air will enter through the latter to fill the vacuum, and the water in the connecting tube will fall back into the second bottle. The gas cannot avoid three separate contacts with water as it passes through the apparatus, so that all of it is sure to be absorbed. In this experiment the gas will be mostly absorbed in the first and second bottles. Test the liquid in the second bottle with red litmus.

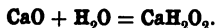
The reaction between the ammonium chloride and the slaked lime is represented by the following equation:—



Ammonium chloride is a compound which may be obtained by bringing together dry ammonia (NH_3) and dry hydrochloric acid gas (HCl),—



It may obviously be regarded as a compound of the group called *ammonium* (NH_4) with the element chlorine. From this view is derived the name *ammonium chloride*. Slaked lime (calcium hydroxide) is prepared by adding water to quicklime, which is chemically the oxide of the metal calcium,—



The compound of nitrogen and hydrogen known as *hydrazoic acid* or *azoimid* (N_3H) is distinctly acid in its properties. We have here an interesting instance of two compounds of the same elements, one of which is strongly basic, the other an acid. The instability of hydrazoic acid is also in marked contrast with the stability of ammonia: it decomposes with explosive violence at ordinary temperatures.

CHAPTER VII.

HYDROCHLORIC ACID.

78. **Muriatic** (sea salt) or **hydrochloric acid** is a liquid which has been known for centuries, and is to-day an article of commerce largely employed in the useful arts. The pure acid is a *gas*, as ammonia is. The liquid muriatic acid of commerce is only an aqueous solution of this gas, and gives it up, when heated, precisely as ammonia water yields ammonia gas.

This operation may be conveniently performed in the apparatus shown in Fig. 20. About

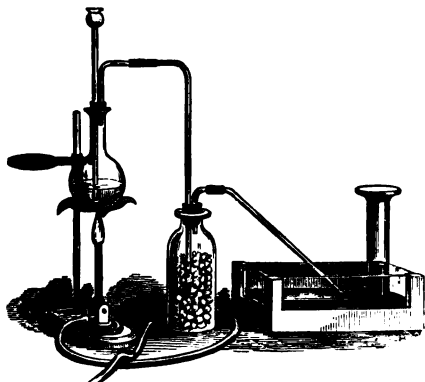


Fig. 20.

250 cc. of the commercial acid is poured into the flask, which is then moderately heated. The gas disengaged is charged with aqueous vapor, which needs to be removed before the gas is collected. For this purpose the delivery tube is carried to the bottom of a bottle filled with pieces of pumice stone saturated with strong sulphuric acid. The moisture of the gas is greedily absorbed by the large surface of acid with which the gas comes in contact as it is forced upward through the acid-soaked stone. The dry, colorless transparent gas can best be collected over mercury, for it is extremely soluble in water; or, as it is heavier than air, it may be collected in bottles or jars by downward displacement. In this case the bottle or jar will be known to be filled with the gas by the abundant escape of dense white fumes, which are produced by its union with the moisture of the air.

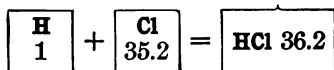
The gas is strongly acid in taste and reaction on vegetable colors, provokes violent coughing, and is wholly irrespirable.

It is neither combustible, nor will it support combustion. The gas is somewhat heavier than air, and is very soluble in water. At 0°, one volume of water dissolves about five hundred volumes of the gaseous acid. It may be condensed to a liquid with some difficulty.

Exp. 40.— Out of doors, or in a strong draught of air, fill a perfectly dry flask, of about 1 l. capacity, with the gas, by downward displacement. Slowly withdraw the tube which delivers the gas, so that the space occupied by the tube may be filled by gas, and not by air. Close the flask with the thumb or with a cork, invert the flask, and open it under water. Water will rush in with great violence to combine with the hydrochloric acid.

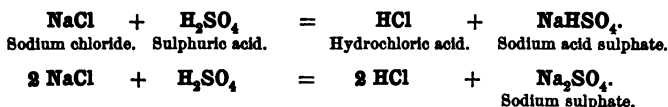
The injurious action of hydrochloric acid gas upon vegetation is probably due to its attraction for water. If a spray of fresh leaves be placed in a bottle of the gas, they will become brown and shriveled at once.

79. The composition of the gas has been determined both by analysis and by synthesis; and it has been found that one volume of hydrogen is combined with one volume of the elementary gas chlorine (Cl) to form two volumes of hydrochloric acid. The molecule of hydrochloric acid will be represented by the formula HCl ; and, as the vapor density of chlorine—that is, the weight of any volume compared with the weight of an equal volume of hydrogen, under the same conditions of temperature and pressure—is 35.2, the following diagram represents the composition of this important compound, both by volume and by weight:—



80. The muriatic acid of commerce is usually made from the most abundant and cheapest of all the natural compounds of chlorine,—common salt, whose chemical name is *sodium chloride*, and whose formula is NaCl . This substance supplies the chlorine: the necessary hydrogen is obtained from common sulphuric acid (oil of vitriol), whose composition, as expressed in its formula H_2SO_4 , we have already become familiar with. The reaction may differ according to the proportion of

sulphuric acid employed, for either of the reactions expressed in the following equations may occur:—



In the first of these reactions, only one half of the hydrogen in each molecule of sulphuric acid is replaced by sodium: in the second, both atoms of hydrogen are thus replaced. The first reaction requires more sulphuric acid in proportion to the amount of the product than the second, but is accomplished with less wear of the apparatus, because a more moderate heat suffices for the first than for the second reaction, and because a fusible residue is obtained which can easily be removed from the apparatus.

On the manufacturing scale, the salt and acid are heated in large iron pans or cylinders, and the evolved gas is absorbed by water contained in a series of stoneware Woulfe bottles; or the salt and acid are heated together in furnaces of a peculiar structure, and the gaseous acid is absorbed by being caused to pass up towers packed with pieces of coke or fire brick, over which a current of water flows. Practically, the amount of sulphuric acid employed is intermediate between the quantities required for the reactions above given; and the residue obtained is in a semiliquid condition when warm. This substance, an impure mixture of sodium sulphate and sodium acid sulphate, is known as *salt cake*. The ordinary commercial acid contains from 30 to 40 per cent by weight of real acid.

Exp. 41.—Place 30 g. of dry (or, better, fused), coarsely powdered salt in a flask of a liter capacity, provided with a delivery tube which



Fig. 21.

can be conveniently connected, by a caoutchouc connector, with a series of small Woulfe bottles, such as is represented in Fig. 21. Pour 50 g. of strong sulphuric acid upon the salt, and immediately cork the flask, place it upon a sand bath on the iron stand, and connect the delivery tube with the Woulfe bottles. The tubes by which the gas enters the bottles should barely dip beneath the water contained in them, inasmuch as the solution of

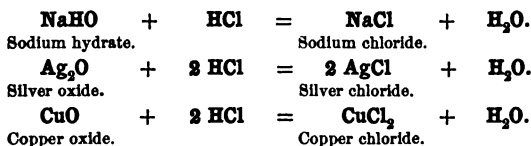
hydrochloric acid is heavier than water. The bottles should not be more than half full, for the water becomes hot, and increases considerably in

bulk. As hot water holds less gas in solution than cold water, it is not amiss to place each three-necked bottle in a vessel of cold water. The first Woulfe bottle should contain but a small quantity of water, and the tube coming from the flask should not dip into this water. The contents of the flask must be *very gradually* and moderately heated, else a violent frothing is liable to occur, which would spoil the experiment. The acid will be purer in the second bottle than in the first, in the third than in the second, and so forth. Add to some bits of granulated zinc in a test tube 10 cc. of the liquid in the second bottle, and see if hydrogen is set free.

81. The uses of hydrochloric acid are very numerous: it is employed in making chlorine, potassium chlorate, and "chloride of lime" (bleaching powder); in preparing ammonium chloride and tin chloride; in the manufacture of gelatin; for dissolving metals, either by itself or mixed with nitric acid; and it is one of the most useful reagents in the analytical laboratory.

82. Hydrochloric acid, as has already been stated (§ 70), differs from the other acids with which we have become acquainted in that it contains no oxygen.

As there are certain compounds called *nitrates* whose formulas may be derived from that of *nitric acid* by replacing the symbol of hydrogen in the acid by that of some metallic element, so there is a series of compounds the formulas of which may be derived from that of *hydrochloric acid* by putting the symbol of a metallic element in the place of the symbol of hydrogen in the acid. These compounds are called *chlorides*: thus sodium chloride (common salt) is **NaCl**. Chlorides are formed in some cases by treating the metal with hydrochloric acid, as in the formation of zinc chloride (**ZnCl₂**), Exp. 18, § 37: in other cases they are formed by treating the oxide or the hydroxide of the metal with hydrochloric acid, as may be seen in these equations:—



83. **Aqua Regia** ("Royal Water").—This name was given by the alchemists to a mixture of hydrochloric and nitric acids, because of its power to dissolve gold, the "king of metals."

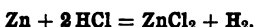
Exp. 42.—Place a few square centimeters of genuine gold leaf at the bottom of a test tube, and pour upon the gold a little strong hydrochloric acid; put some gold leaf in a second test tube, and pour

upon it a few drops of nitric acid. Neither acid attacks the gold, which remains undissolved. If the contents of the two test tubes be mixed together in either tube, the gold leaf will almost immediately dissolve.

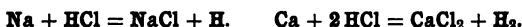
The efficacy of aqua regia as a solvent of gold depends upon the fact that the nitric and hydrochloric acids mutually decompose each other. Chlorine is set free, and, as it issues from its combination with hydrogen, acts on the gold much more energetically than it would in its ordinary condition. The chlorine in this case is said to be in the *nascent* state.

There are numerous cases in which bodies which do not react readily under ordinary conditions are capable of chemical combination at the instant when they are disengaged from other compounds, and the phenomenon finds explanation in the view that molecules under ordinary conditions contain more than one atom (§ 169). When chemical change occurs between molecules, there is, first of all, decomposition of the molecules, and then a rearrangement of the constituent atoms to form new molecules. But an appreciable instant of time must elapse while the atoms are falling into the new arrangements; and during their *nascent*, momentary freedom, the atoms may act as individuals, and be better able to enter into combination than when held in restraint by the forces which ordinarily bind them in the molecule.

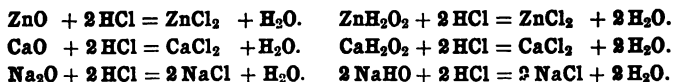
84. Hydrochloric Acid may act on the Elements in Several Ways.—Many elements react with the acid by simply replacing its hydrogen, as has been seen in the preparation of hydrogen by the action of the acid upon zinc, —



So, also, sodium and calcium act in a similar manner, —



Again, there are many elements which do not react in this way. Sulphur, nitrogen, phosphorus, and carbon may be taken as examples. A division of the elements may be made into two classes, — first, those which, when acted upon by hydrochloric acid, take the place of the hydrogen of the acid, and combine with the chlorine, forming chlorides; and, second, those which are not acted upon by hydrochloric acid. When the oxides and hydroxides of the elements of the first class are acted upon by hydrochloric acid, the same chlorides are formed, and water is set free; thus, —

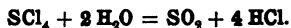


It appears, then, that there are some elements upon which hydrochloric acid acts, with formation of chlorides and evolution of hydrogen, and that upon the oxides and hydroxides of these elements it reacts to form chlorides and water. These elements are known as the *metallic* or base-forming elements.

On the other hand, if the chlorides of those elements which are not acted upon by hydrochloric acid are formed by some other method, as, for example, by treating the element directly with chlorine (Exp. 48, § 97),—and most of them can be prepared in this way,—they will be found to differ from the chlorides of the metals, and especially in their reactions with water. Thus the compound of phosphorus and chlorine known as *phosphorus trichloride* reacts with water, as is represented in the following equation:—



and the chloride of sulphur reacts as follows:—



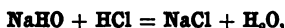
So, also, when the chlorides of other elements of this class react with water, there are formed, as a rule, the oxides or hydroxides of the elements, together with hydrochloric acid.

Elements whose chlorides are thus decomposed by water are classified as the *nonmetallic* or acid-forming elements. In general, the chloride of a nonmetallic or acid-forming element reacts with water to form an oxide or hydroxide of the element, while hydrochloric acid is set free.

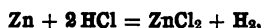
85. Valence.—If the formulas of several of the chlorides which have been mentioned in this chapter be compared, a remarkable difference will be observed. We may take, for examples, hydrogen chloride (HCl), sodium chloride (NaCl), zinc chloride (ZnCl_2), calcium chloride (CaCl_2), and phosphorous chloride (PCl_3). Now, according to the *atomic theory*, these expressions mean that the molecule of hydrochloric acid consists of an atom of hydrogen combined with an atom of chlorine, that the molecule of sodium chloride consists of an atom of sodium combined with an atom of chlorine, that the molecule of calcium chloride contains an atom of calcium and two atoms of chlorine, and that the molecule of phosphorous chloride consists of an atom of phosphorus and three atoms of chlorine. It appears thus that the atoms of hydrogen, and also the atoms of sodium, can hold in combination or fix a single atom of chlorine, that the atoms of calcium can hold two atoms of chlorine, and that the atom of phosphorus, in the compound

represented, can hold three times as many atoms of chlorine as the hydrogen atom can. It will be seen on subsequent pages that other elements differ from one another in a similar way. In speaking of the atom-fixing power, or *valence*, of the elements, it is customary to refer to the hydrogen atom as unity, since, in so far as relates to the number of atoms it can hold, no other element has a smaller power than hydrogen. Thus any element, such as chlorine, whose atom can hold in combination a single atom of hydrogen, is said to have a valence of one, or to be *univalent*; while an element which, like calcium, can combine with two atoms of a univalent element, is said to have a valence of two, or to be *bivalent*; etc. The valence of an atom is sometimes indicated by small Roman numerals printed above the symbol, as $\overset{\text{I}}{\text{H}}$, $\overset{\text{II}}{\text{Ca}}$, $\overset{\text{IV}}{\text{C}}$, etc.; or by accents attached to the symbol, as H' , Ca'' , C''' , etc.

86. Replacing Power.—In the formation of salts of the several acids, it has been seen in such cases as where sodium chloride was prepared by the reaction of hydrochloric acid on sodium hydroxide,



that the hydrogen of the acids is replaced by metallic atoms, and that one atom of a univalent element takes the place of an atom of hydrogen. In the formation of sodium sulphate, two atoms of the univalent element take the place of two atoms of hydrogen; while in the formation of zinc chloride,



one atom of the bivalent element takes the place of two atoms of hydrogen; so also, in the formation of copper nitrate, $\text{Cu}(\text{NO}_3)_2$, from nitric acid, the bivalent atom of copper replaces two atoms of hydrogen in two molecules of the acid. The number of atoms of hydrogen which an element can replace depends upon the valence of that element. This matter of valence, or atom-fixing power, will be more fully discussed in a subsequent chapter.

87. Chemical Calculations.—If we know the reactions involved, and the atomic weights of the elements, it is a simple matter to calculate the amount of material required to produce a given weight of any substance, or the quantity of the substance produced by the decomposition of a known weight of the material. In the manufacture of hydrochloric acid, for

instance, suppose it were required to ascertain how much sulphuric acid would be necessary to decompose 100 kilo. of salt, bearing in mind that the result may be effected according to either of the two reactions formulated in § 80.

| | | | | | |
|-------------------------|-------------|----|-------------------------------------|----|------------------------|
| The molecular weight of | NaCl | is | 23 + 35.2 | = | 58.2 |
| " | " | " | H₂SO₄ | is | 2 + 32 + (4 × 16) = 98 |
| " | " | " | NaHSO₄ | is | 23 + 1 + 32 + 64 = 120 |
| " | " | " | Na₂SO₄ | is | 46 + 32 + 64 = 142 |
| " | " | " | HCl | is | 1 + 35.2 = 36.2 |

The weight of the sulphuric acid needed in the two cases is ascertained by solving the following proportions:—

| | | | | | | | | |
|-----------------|---|-----------------|---|------------------------------------|---|---------------------|---|--|
| First reaction | } | 58.2 | : | 98 | = | 100 | : | $x (= 168.39)$ |
| | | <i>Mol. wt.</i> | | <i>Mol. wt.</i> | | <i>No. of Kilo.</i> | | <i>No. of Kilo.</i> |
| | | NaCl | | H₂SO₄ | | NaCl used. | | H₂SO₄ needed. |
| Second reaction | } | 116.4 | : | 98 | = | 100 | : | $x (= 84.19)$ |
| | | <i>Mol. wt.</i> | | | | | | |
| | | 2 NaCl | | | | | | |

The weight of hydrochloric acid gas produced in the two cases will be precisely the same: it is deduced from the proportions,—

| | | | | | | | | |
|-----------------|---|-----------------|---|-----------------|---|------------------|---|----------------------|
| First reaction | } | 58.2 | : | 36.2 | = | 100 | : | $x (= 62.2)$ |
| | | <i>Mol. wt.</i> | | <i>Mol. wt.</i> | | <i>Kilo.</i> | | <i>Kilo.</i> |
| | | NaCl | | HCl | | NaCl used | | HCl produced. |
| Second reaction | } | 116.4 | : | 72.4 | = | 100 | : | $x (= 62.2)$ |
| | | <i>Mol. wt.</i> | | <i>Mol. wt.</i> | | | | |
| | | 2 NaCl | | 2 HCl | | | | |

The weights of the residual sodium salts in the two cases may be deduced as follows:—

| | | | | | | | | |
|-----------------|---|-----------------|---|-------------------------------------|---|------------------|---|---|
| First reaction | } | 58.2 | : | 120 | = | 100 | : | $x (= 205.24)$ |
| | | <i>Mol. wt.</i> | | <i>Mol. wt.</i> | | <i>Kilo.</i> | | <i>Kilo.</i> |
| | | NaCl | | NaHSO₄ | | NaCl used | | NaHSO₄ |
| Second reaction | } | 116.4 | : | 142 | = | 100 | : | $x (= 121.99)$ |
| | | <i>Mol. wt.</i> | | <i>Mol. wt.</i> | | | | <i>Kilo.</i> |
| | | 2 NaCl | | Na₂SO₄ | | | | Na₂SO₄ produced. |

A general rule may be formulated for the solution of all such problems. Write the reaction in the form of an equation; make then the proportion :—

As the symbol of the given substance is to the symbol of the required substance, so is the weight of the given substance to the weight of the required substance. Then,

Give the symbols their proper numerical value, and calculate from these figures the unknown quantity.

An example may illustrate the application of this rule. We have given to us 6.608 g. of copper, and wish to know (a) how much nitric acid (HNO_3) is required to dissolve it, and (b) how much nitric oxide (NO) will be formed during the process of solution. Expressing the reaction in the form of an equation, we have,—



and expressing it as a proportion, we have, symbol of the given substance (3 Cu) : symbol of required substance (8 HNO_3) = weight of given substance (6.608 g.) : weight of required substance (x g.).

If, now, we reduce the symbols to numbers, by adding together the atomic weights which they represent, we will have for (a)—

$$189 : 504 = 6.608 : x \text{ g.} = \text{Ans. } 17.62 \text{ g. of nitric acid};$$

and for (b)—

$$189 : 60 = 6.608 : x \text{ g.} = \text{Ans. } 2.09 \text{ g. of nitric oxide};$$

and if we wish to know the volume of gas set free, we need only to divide the weight of the gas obtained by the weight of one liter of the gas.

It is, of course, oftentimes not necessary to express reaction. For instance, suppose we wish to know how much chlorine could be obtained from 172.5 g. of hydrochloric acid gas (HCl). HCl represents one molecule of hydrochloric acid, or 36.2 parts by weight, containing 35.2 parts by weight of chlorine. We have, then, the proportion $36.2 : 35.2 = 172.5 : x$; for there will be the same amount of chlorine relatively in the 172.5 g. as there is in the 36.2 parts representing the weight of the molecule, namely, 167.7 g. In a similar manner we can readily determine by a simple proportion the weight of any constituent of a compound.

88. Percentage Composition.—The method of calculating the percentage composition of a compound from its symbol is equally simple. First determine the molecular weight by adding together the weights of the atoms comprising the molecule. Thus the formula of sodium sulphate is Na_2SO_4 : its molecular weight, then, is $46 + 32 + 64 = 142$. In 100 parts by weight of the substance, the

elements will necessarily exist in the same relative proportion as they do in the molecule, the weight of which is 142. Hence all that needs to be done in order to determine the per cent (%) of each of the elements present is to write out the simple proportion, as the weight of the molecule is to the weight of any element in the molecule, so is 100 to the per cent. Thus: —

$$\begin{array}{ll} 142 : 46 = 100 : x. & x = 32.39 \% \text{ sodium.} \\ 142 : 32 = 100 : y. & y = 22.54 \% \text{ sulphur.} \\ 142 : 64 = 100 : z. & z = 45.07 \% \text{ oxygen.} \end{array}$$

CHAPTER VIII.

THE HALOGENS: FLUORINE, CHLORINE, BROMINE, AND IODINE.

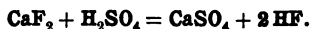
FLUORINE (F). — ATOMIC WEIGHT, 19.

89. Fluorine occurs in nature in large quantities, and is widely distributed, but always in combination with other elements. It is found chiefly in combination with calcium in the mineral called *fluor spar* (calcium fluoride, CaF_2). A considerable mine of a fluorine mineral called *cryolite* (a fluoride of sodium and aluminum, Na_3AlF_6) is worked in Greenland. Small quantities of fluorine are found in several other minerals also.

90. Fluorine cannot readily be obtained in the free state, and little is known of it in that condition. Of all the elements, it appears to have the strongest tendency to enter into chemical combination. It acts upon almost all substances at ordinary temperatures. It is not only difficult to expel fluorine from the minerals in which it is found in nature; but, on being set free from one compound, it immediately attacks whatever substance is nearest at hand, and so enters into a new combination: hence the great difficulty of collecting it. It is a pale yellow gas, of strong and disagreeable odor. No doubt is entertained as to the general nature of fluorine, since its compounds are closely analogous in many respects to the corresponding compounds of chlorine, bromine, and iodine. It

is to be remarked that fluorine is the only element known which forms no compound with oxygen.

91. **Hydrofluoric Acid (HF).**— With hydrogen, fluorine forms a powerful acid corresponding to hydrochloric acid and the other hydrides of the halogen group. It is a more energetic acid than either of the others, but is specially characterized by its corrosive action upon glass. It may be readily prepared by treating powdered fluor spar with strong sulphuric acid, the reaction being analogous to that which occurs when common salt is heated with sulphuric acid, —



Since the acid rapidly disintegrates glass, the process must be conducted in metallic vessels. Ordinarily, retorts of lead or platinum are employed, and the distillate is collected in receivers made of the same metals, and carefully cooled by means of ice.

The acid thus prepared always contains a small amount of water which it is difficult to remove completely. The *perfectly dry* acid, which may be made by the distillation of dry potassium acid fluoride (KHF_2), is, like that prepared as above, a very volatile, fuming liquid; it does not, however, act upon glass. Upon the metals, or base-forming elements, an aqueous solution of hydrofluoric acid acts similarly to hydrochloric acid. The concentrated aqueous solution fumes in the air as concentrated hydrochloric acid does, and, on being heated, the gaseous acid escapes from it. Both the vapor and the solution are poisonous. Great care should always be taken in using the acid, as it is extremely corrosive, producing, by its action on the tissues, painful sores exceedingly difficult to heal. Vessels of lead, platinum, leather, or ceresine, are employed for the preservation of the acid, as they are but little affected by it.

This corrosive power possessed by moist hydrofluoric acid gas, as well as by its aqueous solution, is made use of for etching glass. The graduations on the glass stems of thermometers and eudiometers may thus be made with great precision and facility. The acid is largely employed also in ornamenting glass with etched patterns.

Exp. 43. — Warm a slip of glass, and rub it with beeswax so that it shall be everywhere covered with a thin, uniform layer of the wax. With a needle, or other pointed instrument, write a name, or trace any outline through the wax, so as to expose a portion of the glass. Lay the etching, face downward, upon a bowl or trough of sheet lead, in which has been placed a teaspoonful of powdered fluor spar and enough strong sulphuric acid to convert it into a thin paste.

Cover the glass and the top of the dish with a sheet of paper, and then gently heat the leaden vessel for a few moments, taking care not to melt the wax; then set the dish aside in a warm place, and leave it at rest during an hour or two. Finally melt the wax, and wipe it from the glass with a rag or a piece of paper. The glass will be found to be etched and corroded at the places where it was laid bare by the removal of the wax.

CHLORINE (Cl). — ATOMIC WEIGHT, 35.2.

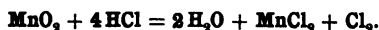
92. Chlorine is an abundant element, and very widely distributed in nature; but it never occurs in the free state, for the reason that it combines very readily with other substances. It exists chiefly in combination with sodium as common salt (sodium chloride), which is obtained by evaporating sea water or the water of saline springs, or by mining the beds of rock salt which occur in many localities. Every liter of sea water could be made to yield five liters of chlorine gas by the decomposition of the chlorides dissolved in it. Beside sodium chloride, sea water contains small quantities of the chlorides of several other metals: there are numerous minerals, also, which contain chlorine.

93. Chlorine can readily be prepared from hydrochloric acid by removing the hydrogen of that acid by chemical means.

Exp. 44. — In a flask of about 500 cc. capacity (Fig. 22), furnished with a suitable delivery tube, place 8 or 10 g. of coarsely powdered manganese dioxide; pour upon it 20 or 30 g. of common hydrochloric acid, and *gently heat* the mixture. Chlorine will soon be disengaged, and may be recognized by its peculiar color. It may be dried by passing it through a tube filled with calcium chloride (Exp. 46, § 96), or by the use of sulphuric acid, as in the preparation of dry hydrochloric acid. The color of the gas easily shows when the vessel employed to collect it is full. The gas may be kept for some time in jars if the stoppers or glass plates covering them are ground and greased. Being very heavy, the gas may best be collected by displace-

ment in dry bottles placed in the open air or in a case or box provided with an efficient draught. It may also be collected over warm water or brine in the water pan. It cannot be well collected over water at the ordinary temperature, since it is rather easily soluble therein; though the difficulty may be obviated in part by evolving the gas rapidly, or by passing the delivery tube to the top of the bottle in which the gas is collected. It must not be left standing over water, since it would soon be entirely absorbed. In experimenting with chlorine, care must always be taken not to inhale it.

The reaction which occurs in this experiment may be thus formulated:—



This equation represents the final result, though the actual changes which take place are probably much more complex. The general action of hydrochloric acid upon a dioxide is to form the chloride of the metal and water, and to set free chlorine.

Manganese dioxide is a substance rich in oxygen, which, under certain conditions, it readily yields up to other elements. In the case before us, the oxygen of the manganese dioxide unites with the hydrogen of the hydrochloric acid to form water. The chlorine of the hydrochloric acid unites in part with the manganese to form manganese chloride, and is in part left free.

94. At the ordinary temperature, chlorine is a gas of yellowish green color, about 2.5 times heavier than atmospheric air. A liter under standard conditions weighs 3.167 g. Its vapor density and atomic weight are 35.2. It is excessively irritating and suffocating, even when inhaled in exceedingly small quantities. It acts upon the mucous membrane of the throat and nose to produce an effect much like that of a cold in the head. Any attempt to breathe the undiluted gas would undoubtedly be fatal. The aqueous solution of the gas known as *chlorine water* possesses many of the properties of the free gas. It is frequently employed for laboratory uses as a substitute for the gas.

95. Chlorine is a powerful chemical agent. It combines with hydrogen with explosive violence when a mixture of equal volumes of the two gases is heated, or even exposed to sunlight.

Exp. 45.—In a soda-water bottle, which must be screened from strong light by wrapping it in a towel, unless direct and reflected sun-

light be excluded from the room, mix equal volumes of chlorine and hydrogen by first filling the bottle, over water, half full with chlorine gas, and then with hydrogen. Cork the bottle, and let it stand with its mouth under water for a few moments, so that the gases may mix thoroughly; then remove the cork and hold the mouth of the bottle in the flame of a lamp. A sharp explosion will ensue, and, on placing a bit of blue litmus paper in the bottle, it will be turned red by the hydrochloric acid formed.

A mixture of the two gases may be kept in the dark for any length of time without change. In diffused daylight they usually unite only slowly and gradually; but in direct sunlight their union is so instantaneous as to be attended with explosion.

96. Chlorine combines also very readily with many of the metals, the combination being in several instances attended with evolution of light.

Exp. 46. — Pour enough warm sand into a bottle of at least half a liter capacity to cover the bottom of the bottle, and fill the bottle with dry chlorine gas by displacement. Gradually sift a gram or two of very finely powdered metallic antimony into the bottle. The metal will instantly take fire, and fall in a glowing state to the bottom of the bottle. This fire attends the formation of antimony trichloride, a portion of which will be seen pervading the bottle as a white smoke.

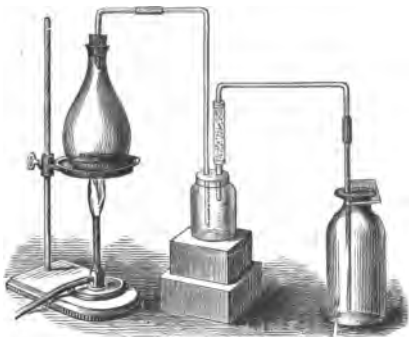
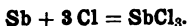


Fig. 22.



It is necessary, for the success of this experiment, that the gas be thoroughly dried. This is effected by heating the flask containing the manganese dioxide and hydrochloric acid *gently*, and passing the chlorine through a tube filled with calcium chloride (Appendix, § 16). It is not amiss to interpose a small bottle between the flask and the drying tube. This bottle may be kept cool by immersion in water, and will retain a considerable portion of the moisture carried forward by the gas.

This experiment, and, indeed, all experiments with chlorine, should be performed only in places where there is a current of air sufficiently

powerful to carry away from the operator the volatile products of the reaction, together with any chlorine which may escape from the bottle. The delivery tube should reach to the bottom of the vessel in which the gas is collected; and the mouth of the vessel should be covered with a piece of paper, to prevent currents of air from carrying away the chlorine.

As in the case of the union of sulphur with copper (Exp. 1, § 2), so here it will be seen that *burning*, as commonly understood, is in no wise peculiar to the union of oxygen with the other elements. In the act of chemical combination, heat is always evolved, and, of course, light as well, if particles of solid matter be present, and become hot enough to be luminous.

Since oxygen is very abundant, we are more accustomed to witness exhibitions of its chemical action than of that of any other element; but we must not, therefore, lose sight of the fact that among the elements there are several which possess chemical power as great (when brought into play), though not as frequently exhibited, as that of oxygen.

97. Introduce into a jar containing dry chlorine a burning jet of hydrogen. It will continue to burn with a peculiar green light, the two gases uniting to form hydrochloric acid, and dense white fumes having an acid reaction will be noticed. By reversing the experiment, chlorine may just as well be burned in an atmosphere of hydrogen. Although chlorine is thus both combustible and a supporter of combustion, as far as *hydrogen* is concerned, it does not unite directly with either *oxygen* or *carbon*.



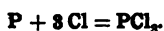
Fig. 23.

If a bit of paper attached to a wire be dipped in hot oil of turpentine, and then quickly plunged into a bottle of chlorine, it will usually take fire spontaneously, and burn with evolution of dense black fumes. On account of the volatility and ready inflammability of oil of turpentine, it is best heated upon a water bath (Appendix, § 17), in a porcelain dish.

Exp. 47. — Thrust a burning taper, or a bit of flaming wood or paper, into a bottle of chlorine gas. The flame will become murky, and, after struggling for a moment, will go out. Much smoke is at the same time given off. The wax, wood, paper, and turpentine of the foregoing experiments,

and, indeed, most of the substances ordinarily used as combustibles, contain hydrogen and carbon. The hydrogen of these substances will burn in chlorine, that is, will unite chemically with the chlorine to form hydrochloric acid; but the carbon will not thus unite with chlorine. Hence it is that in the experiments in question the combustion is at the expense of the hydrogen; the hydrogen of the candle, turpentine, and so forth, alone unites with chlorine; while the carbon is set free as lampblack or smoke.

Exp. 48. — Place a bit of dry phosphorus in a deflagrating spoon, and immerse it in a bottle of the dry gas. It will take fire spontaneously, combining with the chlorine to form phosphorus trichloride, —



Many other substances unite with chlorine at ordinary temperatures, with evolution of light and heat, to form chlorides.

98. Chlorine is a powerful *bleaching agent*, and on this account is of great importance in the arts. The chlorine to be used for this purpose must be moist: perfectly dry chlorine will not bleach.

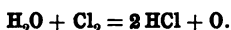
This fact may be illustrated by passing perfectly dry chlorine through a glass tube filled with bits of colored calico. The coloring matters will not be destroyed so long as they remain dry; but if, after the dry chlorine has been allowed to act for a few minutes, a little water be poured into the tube, so that its contents may be moistened, they will be bleached at once.

Those coloring matters which are of vegetable or animal origin are, for the most part, complex compounds of carbon, hydrogen, nitrogen, and oxygen. When moist chlorine is brought into contact with them, a somewhat complicated reaction occurs. A portion of their hydrogen is, no doubt, taken out by the chlorine; but, at the same time, some of the water which is present is decomposed, and its oxygen assists the disorganization of the compound which is to be destroyed. As a rule, the coloring matters are far more easily oxidized than the cotton cloth: hence they can readily be removed by the action of chlorine without injury to the cloth. But, if the action of the chlorine were to be continued after the coloring matter had been destroyed, the cloth itself would gradually be decomposed.

The bleaching properties of chlorine may be conveniently illustrated by means of an aqueous solution of chlorine (*chlorine water*), which may be prepared by connecting the flask in which the gas is generated with a series of Woulfe bottles, as in the preparation of hydrochloric acid (Fig. 21, § 80).

Exp. 49. — Pour into a small bottle a quantity of chlorine water, drop into it a small quantity of a solution of indigo, and stir the mixture with a glass rod. The blue color of the indigo will be immediately destroyed.

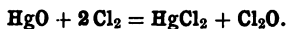
In the same way, the color of litmus, cochineal, anilin purple, or of flowers, calico, and the like, can be readily destroyed by immersion in chlorine water, which has but little action upon mineral colors. Chlorine decomposes water according to the reaction —



This decomposition can be illustrated by filling a long tube with strong chlorine water, and inverting it in a shallow vessel containing some of the same solution. On being placed in direct sunlight, the yellowish green color of the liquid will gradually disappear, and a colorless gas will collect in the upper part of the tube, which, on being tested, will be found to be oxygen. On account of this action, bottles of chlorine water should be kept in the dark.

99. Chlorine is also employed as a *disinfectant*. It destroys noxious effluvia, either by acting on them as on coloring matters, or by simply taking away hydrogen, as in the case of hydrogen sulphide, hereafter to be studied.

100. **Oxides and Acids of Chlorine.** — Chlorine does not combine directly with oxygen, but by indirect methods two oxides have been obtained, — *chlorine monoxide* (Cl_2O) and *chlorine dioxide* (ClO_2). Three other oxides are believed to exist; but they have never been isolated, possibly owing to their great instability under ordinary conditions. **Chlorine monoxide** is formed by the action of chlorine on dry mercuric oxide, —



It is an easily liquefiable gas, yellowish brown in color, and exceedingly unstable, readily undergoing spontaneous decomposition into chlorine and oxygen. **Chlorine dioxide** (ClO_2) is a greenish yellow gas of great instability. It can be obtained by gently heating a mixture of potassium chlorate (KClO_3) and concentrated sulphuric acid. Violent explosions occur at temperatures higher than 30° ; so that it is advisable, unless proper precautions are taken, not to pour sulphuric acid upon potassium chlorate.

Exp. 50. — Into a large test tube supported in a holder, put two or three *small crystals* of pure potassium chlorate (KClO_3), and pour in enough strong sulphuric acid to cover them. The crystals at once acquire a red color, and a greenish yellow gas collects in the tube. If a hot iron wire be touched to the gas, it will explode with violence. Be careful to have the mouth of the tube during the whole experiment turned away from all present. Combustible substances burn in chlorine dioxide with great vigor. This action may be shown by the following experiment.

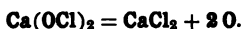
Exp. 51. — Pour into a conical test glass 25 to 30 cc. of water, and throw into the water some scraps of phosphorus, weighing together not more than 0.3 g., and 3 or 4 g. of crystals of potassium chlorate. By means of a thistle tube, bring 5 or 6 cc. of strong sulphuric acid into immediate contact with the chlorate at the bottom of the glass. Then withdraw the thistle tube. In a moment the phosphorus is kindled, and burns with vivid flashes of light beneath the water, the action being due to the liberation of the chlorine dioxide, and the oxidation of the phosphorus by its decomposition.

101. Hypochlorous Acid. — Chlorine monoxide reacts with water to form an acid known as *hypochlorous acid* (HClO). One of the salts of hypochlorous acid, calcium hypochlorite ($\text{Ca}(\text{OCl})_2$), is of great industrial importance, being an ingredient of “chloride of lime” or bleaching powder, which is prepared by passing chlorine gas over layers of slaked lime. This substance is used in very large quantities for bleaching purposes and as a disinfecting agent. It readily gives off chlorine under the influence of chemical agents. When it is treated with an acid, chlorine is disengaged.

Exp. 52. — At the bottom of a large, tall beaker, or other wide-mouthed glass vessel, of the capacity of 2 or 3 l., place a small bottle containing 15 or 20 g. of bleaching powder. Cover the beaker with a glass plate, or sheet of pasteboard, provided with a small hole at the center. Through this hole in the cover pass a thistle tube down into the bottle of bleaching powder, and pour upon it several small successive portions of sulphuric acid diluted with an equal volume of water. Chlorine gas will immediately be set free from the bleaching powder, and, falling over into the bottom of the large beaker, will gradually press out and displace the air therein contained, so that after a short time the beaker will be seen to be completely filled with the green gas. This is by far the easiest and most expeditious method of preparing chlorine. The heavy gas may be ladled out of the jar with a dipper made of a small bottle fastened

to a stick, and poured upon a solution of indigo to show its bleaching power.

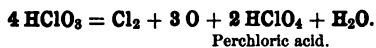
Bleaching powder has the peculiar odor of hypochlorous acid. When it is used for bleaching, it is largely the hypochlorous acid set free from the compound which effects the desired changes. Its solution bleaches, owing to its parting with oxygen.



This change is facilitated by the use of a weak acid whereby hypochlorous acid is liberated, which readily gives up its oxygen, being converted into hydrochloric acid. Goods to be bleached are first run through a solution of bleaching powder, and then through a bath of very dilute sulphuric or hydrochloric acid. A solution containing chloride and hypochlorite of sodium, having great oxidizing power, is called *Labarraque's disinfecting fluid*, or sometimes "*chloride of soda*," and a similar mixture of potassium chloride and hypochlorite is known as *Eau de Javelle*. Both of these liquids are much used in household economy as bleaching agents for removing fruit stains and other colorations from linen and cotton goods.

Exp. 53. — Soak a bit of printed calico in a half liter of water into which 10 or 15 g. of bleaching powder have been stirred. Observe that the color of the calico slowly undergoes change. Then transfer the cloth to another bottle filled with very dilute hydrochloric or sulphuric acid, and take note of the rapidity with which the color is discharged. If need be, again immerse the calico in the bleaching bath, and afterwards in the dilute acid. Finally wash the whitened cloth thoroughly in water.

102. **Chlorous Acid** (HClO_2) is known only in solution. Both the acid and its salts (the chlorites) are unimportant. **Chloric acid** (HClO_3) is very unstable, and readily decomposes, even in aqueous solution, according to the equation —



Corresponding to similar derivations of nitric acid, *chloric acid* gives rise to salts called *chlorates*. **Potassium chlorate** (KClO_3), the most important of these compounds, is prepared by passing chlorine through a warm, concentrated solution of potassium hydroxide, —



It was used in Exp. 4, § 12, as a source of oxygen. Under the influence of heat it is decomposed into oxygen and potassium chloride. The reaction takes place in two stages, potassium perchlorate (KClO_4)

being first formed, which undergoes decomposition when the temperature is increased.



On account of the ease with which it gives up oxygen, potassium chlorate is largely used for the preparation of oxygen and as an oxidizing agent. It is used also, as well as other chlorates, in the manufacture of fireworks. Great care is necessary when working with the chlorates, since they form dangerously explosive mixtures when in contact with combustible substances.

103. **Perchloric acid** (HClO_4), though a more stable body than the other oxygen acids of chlorine, is still very unstable. It is one of the most powerful oxidizing agents known. Its salts are known as the *perchlorates*. The compound *potassium perchlorate*, formed in the first stage of the decomposition of potassium chlorate by heat, can be readily separated from the chloride by treating the mixture with cold water, in which the chloride is readily soluble, while the perchlorate is almost insoluble. If potassium perchlorate is treated with sulphuric acid, perchloric acid can be obtained from the mixture by distillation.

The compounds of chlorine with oxygen and hydrogen form a series, the members of which bear a relation to each other similar to that noticed in the case of the oxides of nitrogen, —

Hypochlorous acid (HClO),
 Chlorous acid (HClO_2),
 Chloric acid (HClO_3),
 Perchloric acid (HClO_4),

the successive members of the series differing from each other by one atom of oxygen. The addition of oxygen to hydrogen and chlorine apparently decreases the stability of the resulting compound; hydrochloric acid (HCl) being very stable, while the oxygen acids are all remarkable for their instability. It is worthy of note that the larger the proportion of oxygen, the greater the stability both of the acids and their salts.

BROMINE (Br). — ATOMIC WEIGHT, 79.4.

104. **Bromine** is an element closely allied to chlorine. It is not found in the free state in nature, but always in combination with some metallic element. *Bromides* occur in small quantities in sea water and in the water of many saline springs. One liter of sea water may be made to yield from 0.0143 to 0.1005 g. of free bromine. *Magnesium bromide* is a constitu-

ent of the uncrystallizable residue, called *bittern*, which remains after the sodium chloride has been crystallized out from the natural brines. At several saline springs this bittern contains so large a proportion of the bromide, that bromine can be profitably extracted from it. Most of the bromine of commerce is thus obtained. The method of preparation is to treat a mixture of a sodium bromide or potassium bromide and manganese dioxide with sulphuric acid.



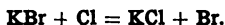
Exp. 54. — Mix half a gram of potassium bromide and a gram of manganese dioxide in a large test tube, and cover the mixture with dilute sulphuric acid. Bromine will be set free as a reddish brown gas, which will rapidly bleach a bit of moistened litmus paper. This experiment should be performed where there is a good draught, as should be all experiments with bromine, since its vapor is exceedingly irritating. Wounds produced when liquid bromine comes in contact with the skin are painful and dangerous.

105. At the ordinary temperature, bromine is a liquid of dark brown-red color, about three times as heavy as water, and highly poisonous. Its odor is irritating and disagreeable, whence the name *bromine*, derived from a Greek word signifying "a stench." It boils at about 60°, but is very volatile even at the ordinary temperature of the air.

Exp. 55. — By means of a small pipette, throw into a flask or bottle of 1 or 2 l. capacity 3 or 4 drops of bromine. Cover the bottle loosely, and leave it standing. In a short time it will be filled with a red vapor, which is bromine gas. This vapor is very heavy, more than 5 times as heavy as air, and rather more than 79 times heavier than hydrogen. Like chlorine, bromine is soluble in water, 1 part dissolving in about 33 parts of water. This aqueous solution is decomposed, like that of chlorine, on exposure to sunlight.

106. In its chemical behavior, as well as in many of its physical properties, bromine closely resembles chlorine, but it is liberated by chlorine from its compounds.

Exp. 56. — Make a solution of a few small crystals of potassium bromide in 5 cc. of water. Add a drop or two of chlorine water. Bromine will be set free, and will color the water.

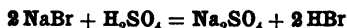


If, now, two drops of carbon disulphide (CS_2) be added, and the tube be shaken, the free bromine will be dissolved by the carbon disulphide, which will take on a deep reddish brown color.

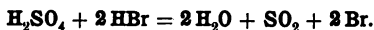
The affinity of bromine for hydrogen, though weaker than that of chlorine, is still powerful. When mixed, the two gases do not combine on mere exposure to sunlight, heat being necessary to bring about their union. Like chlorine, bromine is an energetic bleaching and disinfecting agent, the chemical action of the two elements being similar in kind, though somewhat different in degree. A lighted taper burns for an instant in bromine vapor, and is then extinguished.

If finely powdered metallic antimony be thrown into bromine, violent chemical action takes place. The metal burns as in chlorine, antimony bromide being formed. Similar action takes place in the case of many other substances with which bromine combines directly to form bromides.

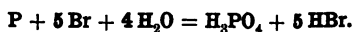
107. Hydrobromic Acid (HBr).—Like chlorine, bromine forms with hydrogen a compound in which equal volumes of the two elements (the bromine being in the state of vapor) are united without condensation. Hydrobromic acid is a colorless, irritating gas, readily soluble in water, forming a strongly acid solution which resembles hydrochloric acid in many respects in its chemical action. It might naturally be expected that this acid could be prepared by a reaction similar to that employed in the preparation of hydrochloric acid; viz., by treating a bromide with sulphuric acid. But strong sulphuric acid decomposes hydrobromic acid, which is less stable than hydrochloric acid; and, although the reaction



does take place, a further reaction, resulting in the decomposition of the hydrobromic acid, occurs:—



Hydrobromic acid is usually prepared by the action of bromine and phosphorus upon each other in the presence of water, the reaction being represented by the equation—



No oxides of bromine have as yet been isolated.

108. **Hypobromous acid** (HBrO) closely resembles the corresponding acid of chlorine (§ 101).

Bromic acid (HBrO_3) is analogous to chloric acid (HClO_3). The *bromates* resemble the corresponding chlorates, and are prepared in a similar manner. No acids of bromine corresponding to chlorous or perchloric acid have as yet been obtained. Bromine and its compounds are used in the analytical laboratory, and in medicine and photography, as well as in the manufacture of certain dyestuffs obtainable from coal tar.

IODINE (I).—ATOMIC WEIGHT, 126.

109. **Iodine**, in its chemical properties, bears a striking resemblance to bromine and to chlorine. Compounds of the element exist in sea water and in many saline and mineral springs. The proportion of iodine in sea water is exceeding small, being even smaller than that of bromine; but iodine is obtained more readily than bromine, for iodine is absorbed from sea water by various marine plants, which, during their growth, collect and concentrate the minute quantities of iodine which the sea water contains, to such an extent that it can be extracted from them with profit.

Iodine is obtained for the most part from seaweeds. On the coasts of Scotland, Ireland, and France the seaweeds which contain iodine are gathered, dried, and burned at a low heat. The organic portions are thus destroyed, and the ashes which contain the mineral constituents, including iodine in the form of iodide of potassium or of sodium, are treated with boiling water, and the solution thus obtained is evaporated. The iodides, being much more soluble than the other constituents of the ash, remain dissolved after most of the other salts have crystallized out, and they can be obtained in a comparatively pure condition by further evaporation. Iodine is set free from these iodides by adding to them some manganese dioxide and sulphuric acid, and gently heating the mixture.



Though solid at the ordinary temperature, iodine is easily vaporized, and the vapor obtained may be condensed in suitable vessels.

Exp. 57.—Place in a test tube a few small crystals of potassium iodide, add 2 g. of manganese dioxide and 2 cc. of concentrated sulphuric acid (H_2SO_4), and warm gently. Iodine will be set free in the

form of a violet vapor, and will condense on the upper portion of the tube in the form of minute crystals.

110. At the ordinary temperature, iodine is a soft, heavy, crystalline solid, of bluish black color and metallic luster. Its specific gravity is 4.6. It vaporizes rather freely at the ordinary temperature of the air, and the more rapidly when it is in a moist condition. Its odor is peculiar, somewhat resembling that of chlorine, but weaker, and easily distinguished from it. It is only slightly soluble in water, but dissolves readily in alcohol, to which it imparts a deep brown color.

The vapor of iodine is of a magnificent purple color, whence the name *iodine*, from a Greek word signifying "violet colored." This vapor is very heavy, nearly 9 times as heavy as air. Its specific gravity referred to hydrogen is 126.

Exp. 58. — Hold a dry test tube in the gas lamp by means of the wooden nippers, and warm it along its entire length, in so far as this is practicable. Drop into the hot tube a small fragment of iodine, and observe the vapor as it rises in the tube. If only a small portion of the tube were heated, the vapor would be deposited as solid iodine upon the cold part of its walls.

111. Solid iodine is never met with in the amorphous, shapeless state in which glass, resin, coal, and many other substances occur. No matter how obtained, its particles always exhibit a definite *crystalline* structure. If the iodine be melted, and then allowed to cool, or if it be converted into vapor, and this vapor be subsequently condensed, crystals will be formed in either case. Iodine has a characteristic strong taste. It colors the skin a yellowish brown, and, when applied externally as a counter irritant, it causes the reduction of some kinds of swellings, and excites the tissues to healthy action. It is a valued medicament; but, when swallowed in the solid state, it acts as an energetic corrosive poison.

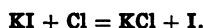
112. A singular property of iodine is its power of forming a blue compound with *starch*.

Exp. 59. — Prepare a quantity of thin starch paste by boiling 30 cc. of water in a porcelain dish, and stirring into it 0.5 g. of starch which has previously been reduced to the consistency of cream by rubbing it in a mortar with a few drops of water.

Pour 3 or 4 drops of the paste into 10 cc. of water in a test tube, and shake the mixture so that the paste may be equably diffused through the water; then add a drop of an aqueous solution of iodine, and observe the beautiful blue color which the solution assumes. If the solution be heated gently, the blue coloration will disappear; but it reappears when the liquid is allowed to cool.

Dip a strip of white paper in the starch paste, and suspend it, while still moist, in a large bottle, into the bottom of which two or three crystals of iodine have been thrown. As the vapor of iodine slowly diffuses through the air of the bottle, it will at last come in contact with the starch, and after some minutes the paper will be colored blue.

This reaction furnishes a very delicate test for iodine. By its means it has been proved that iodine, though nowhere very abundant, is very widely distributed in nature. This reaction is also made the basis of a test for chlorine. Strips of paper are smeared with starch paste into which potassium iodide in solution has been stirred. The paper is dried, and kept in stoppered bottles. When a strip of this paper is moistened and exposed to chlorine gas, the chlorine attacks the potassium iodide, potassium chloride is formed, and iodine is set free. The iodine thus set free manifests itself by imparting the characteristic blue color to the starch, —



Exp. 60. — Put in a test tube 1 g. of manganese dioxide. Pour upon it 1 cc. of concentrated hydrochloric acid, and warm gently. Now hold a piece of moistened iodo-starch paper over the tube and notice the result. If the iodo-starch paper is held too long in contact with the chlorine, the blue color due to the free iodine disappears, owing to oxidation taking place and iodic acid (HIO_3) being formed.

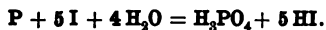
Bromine and chlorine are both capable of replacing iodine and setting it free from its compounds, as can be well illustrated by the following experiment.

Exp. 61. — Put a small quantity of a very dilute solution of potassium iodide in a test tube, add a few drops of carbon disulphide and a few drops of chlorine water, shake the tube, and allow it to stand for a few moments. Repeat the experiment, using bromine water instead of chlorine water. In both cases the carbon disulphide will dissolve the iodine which has been set free from the iodide of potassium, and assume a deep violet color.

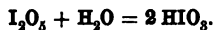
113. As has been already stated, iodine, in its chemical behavior, resembles chlorine and bromine, only its affinities are more feeble. It enters into combination with less energy than either of these elements, and is displaced by them from most of its combinations. Like them, it unites directly with the metals and with several other elements. It gradually corrodes organic tissues, and destroys coloring matters, though but slowly. Iodine and certain of its compounds are much used in medicine and in photography.

114. **Hydriodic acid (HI)** is a colorless gas of suffocating odor, very soluble in water. The aqueous solution has the general properties of hydrochloric acid. The gas is made up of equal volumes of hydrogen and iodine vapor. The proportions by weight are 1 part of hydrogen to 126 parts of iodine. The chemical effect of the small proportion of hydrogen contained in hydriodic acid is most remarkable. Only $\frac{1}{127}$, or less than 1 per cent, of hydriodic acid, is hydrogen; yet this very small proportional quantity of hydrogen is competent to impart to the new compound properties possessed by neither the iodine nor the hydrogen: the acid bears no resemblance to either of its constituents.

Hydrogen and iodine do not readily unite directly: a very high temperature is necessary to cause combination to take place. Even when indirect methods are resorted to, it is less easy to prepare hydriodic than hydrochloric or hydrobromic acid. The method adopted is like that used for the preparation of hydrobromic acid. It consists in treating phosphorus with iodine and water, —



115. **Iodic acid (HIO_3)** is analogous to chloric and bromic acids, but differs from them in being much more stable. It can be made by treating iodine with strong oxidizing agents. It is a crystallized solid, which, when heated to 170° , loses water and yields iodine pentoxide (I_2O_5), which may be regarded as the anhydride of the acid, just as N_2O_5 is the anhydride of nitric acid.



The *iodates* correspond in composition and general character to the bromates and chlorates, but are much more stable bodies,

Iodine pentoxide is a white solid, easily soluble in water. It does not undergo decomposition until heated to 300° . The compound of oxygen and iodine is thus much more stable than any of the oxides of chlorine, the affinity for oxygen of the members of the group increasing as that for hydrogen decreases.

Periodic acid (HIO_4) is analogous to perchloric acid: its salts are formed by the oxidation of iodates or by heating them.

116. Nitrogen Iodide. — Nitrogen forms, with chlorine, bromine, and iodine, a class of compounds which are very explosive. Nitrogen chloride is extremely dangerous, often exploding spontaneously without apparent cause. Nitrogen iodide is much less explosive, and may safely be prepared in very small quantities.

Exp. 62. — Place 0.25 g. of finely powdered iodine in a porcelain capsule, pour upon it enough concentrated ammonia water to somewhat more than cover the iodine, and allow the mixture to stand during 15 or 20 minutes. Collect in several small filters (Appendix, § 15) the insoluble dark brown powder which will be found at the bottom of the liquid. Wash well with cold water, and then remove the filters, together with their contents, from the funnels; pin them upon bits of board, and allow them to dry spontaneously. The powder is nitrogen iodide. As soon as it has become thoroughly dry, it will explode upon being rubbed, even with a feather, or jarred, as by the shutting of a door, or by a blow upon the wall or table.

117. The Halogen Group. — Fluorine, chlorine, bromine, and iodine constitute one of the most remarkable and best-defined natural groups of elements. Whether we regard the uncombined elements or their compounds, it is impossible not to be struck with the close analogies which subsist between them.

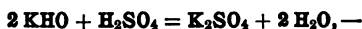
With hydrogen, all of these elements unite in the proportion of one volume to one volume, without condensation, to form acid compounds extremely soluble in water, and possessing throughout analogous properties. Moreover, with the exception of fluorine, each of them forms a powerful acid containing three atoms of oxygen, beside divers other compounds of obvious likeness. With nitrogen, they all form explosive compounds. With metals, the members of the group unite to form saline compounds (such as common salt, NaCl), whence the name *halogens* ("salt formers"). It will be noticed

that there is a marked family resemblance between the four halogen elements as regards their *physical* as well as their *chemical* characteristics; but, with all their properties, a distinct progression is observable from fluorine, through chlorine and bromine, to iodine. At the ordinary temperature, fluorine and chlorine are gases, bromine a liquid, and iodine a solid, though at temperatures not widely apart all but fluorine are known in the gaseous and liquid states.

The specific gravity of bromine vapor is greater than that of chlorine, and that of iodine greater than that of bromine. Fluorine gas is almost colorless, chlorine is a yellowish green gas, the vapor of bromine is reddish brown, and that of iodine violet. So with all their other properties, — fluorine will be at one end of the scale, iodine at the other, while chlorine and bromine invariably occupy intermediate positions.

The properties of the elements constituting this group illustrate a general principle; namely, that, among the members of a natural chemical group, *chemical energy* varies in the inverse direction of the *atomic weights*. Thus the atomic weight of fluorine is 19; that of chlorine is 35.2; that of bromine, 79.4; and that of iodine, 126: while the chemical energy of these elements follows the opposite order, fluorine being the most energetic, and iodine the least so. It will be seen on subsequent pages, that all the elements naturally fall into a few well-marked groups, and that the members of each of these groups resemble one another more or less closely as to their physical and chemical properties, which always vary in the order of the atomic weights.

118. **Halides.** — Originally the term *salt* (§§ 67, 68) was applied not only to sodium chloride, but to any saline substance which bore even a superficial resemblance to common salt; but, with the progress of knowledge, the meaning of the word has been greatly extended and modified. Nowadays the term *salt* as used by chemists does not necessarily imply the old idea of salinity, and there is even a disposition to restrict the word to bodies produced by the action of oxygen acids upon hydroxides of metals, — as when potassium hydroxide reacts with sulphuric acid to form the salt potassium sulphate, together with water,



and to apply the term *halide* to compounds of a halogen and a metallic element. Thus the compounds NaCl , KBr , and CaF_2 are halides. Vast numbers of halides have been described. Some of them unite with others to form double compounds which are analogous in several respects to the salts formed by the reaction of acids and bases that contain oxygen. For example, the mineral cryolite (§ 89) is a double fluoride of sodium and aluminum ($3\text{NaF} \cdot \text{AlF}_3$), and several double chlorides will be mentioned in subsequent chapters. It is to be observed that there is a close analogy between the simple halides and the corresponding hydroxides. Thus common salt (NaCl) is akin to sodium hydroxide (NaOH), in which the group of atoms known as hydroxyl (OH) plays a similar part to the atom of chlorine in sodium chloride. In the same sense, the formula of fluor spar (CaF_2) is related to that of calcium hydroxide ($\text{Ca}(\text{OH})_2$).

CHAPTER IX.

OZONE.

119. Beside ordinary oxygen, such as is found in the air and has been prepared in Exps. 3 and 4, §§ 9 and 12, another kind or form of this element is known to chemists. This new modification of oxygen has received a special name, *ozone*.

Several other elements, notably sulphur, phosphorus, and carbon, occur, as oxygen does, in very unlike states, or with very different attributes, while the fundamental chemical identity of the substance is preserved. The word *allotropism* is employed to express this capability of some of the elements: it is derived from Greek words signifying "of a different habit or character." This word serves merely to bring into one category a considerable number of conspicuous facts, of whose essential nature we have still much to learn. There is, of course, no virtue in the word itself to explain or account for the phenomena to which it refers (compare § 172).

120. Ozone is an exceedingly energetic chemical agent which resembles chlorine in some respects: it can therefore be advantageously studied in connection with the chlorine group.

It was long ago noticed, that, when an electrical machine was put in operation, a peculiar, pungent odor was developed.

More recently it has been observed that the same odor is manifested during the electrolysis of water (§ 27), and that this odor resembles that evolved by moistened phosphorus when exposed to the air. It has gradually been made out, that the odor in each of these cases is due to the presence of a peculiar modification of oxygen, called *ozone* from a Greek word signifying "to smell."

121. Ozone may be best prepared by certain electrical machines devised for the purpose; but the phosphorus method is simple and convenient.

Exp. 63. — In a clean bottle of 1 or 2 l. capacity place a piece of phosphorus 2 or 3 cm. long, the surface of which has been scraped clean (under water) with a knife; pour water into the bottle until the phosphorus is half covered; close the bottle with a loose stopper, and set it aside in a place where the temperature is 20° or 30°. In the course of 10 or 15 minutes a column of fog, due to the formation of some hydrogen dioxide, will be seen to rise from that portion of the phosphorus which projects above the water; the original garlic odor of the phosphorus will soon be lost; and the peculiar odor of ozone will gradually pervade the bottle. After one or two hours, the bottle will be found to contain an abundance of ozone for purposes of illustration.

The chemical changes which occur during this experiment are complicated. It will be enough to say of them, that the phosphorus unites with oxygen from the air in the bottle to form an oxide of phosphorus; that during this process of oxidation a portion of the oxygen in the bottle is changed into ozone; and that some of the ozone remains, even after several hours, diffused in the air of the bottle.

It must be distinctly understood that only a very minute quantity of ozone is obtained in the foregoing experiment; but ozone is a substance possessing great chemical power, and but little of it is needed in order to exhibit its characteristic properties.

122. Ozone is an irritating, poisonous gas, which at extremely low temperatures may be compressed to a dark blue liquid. Air which is highly charged with ozone is irrespirable, and produces effects on the human subject similar to those produced by chlorine. Its odor, which has been compared to that of weak chlorine, is so powerful that it can be recognized in air containing only one millionth part of the gas. Like

108. **Hypobromous acid** (HBrO) closely resembles the corresponding acid of chlorine (§ 101).

Bromic acid (HBrO_3) is analogous to chloric acid (HClO_3). The *bromates* resemble the corresponding chlorates, and are prepared in a similar manner. No acids of bromine corresponding to chlorous or perchloric acid have as yet been obtained. Bromine and its compounds are used in the analytical laboratory, and in medicine and photography, as well as in the manufacture of certain dyestuffs obtainable from coal tar.

IODINE (I).—ATOMIC WEIGHT, 126.

109. **Iodine**, in its chemical properties, bears a striking resemblance to bromine and to chlorine. Compounds of the element exist in sea water and in many saline and mineral springs. The proportion of iodine in sea water is exceeding small, being even smaller than that of bromine; but iodine is obtained more readily than bromine, for iodine is absorbed from sea water by various marine plants, which, during their growth, collect and concentrate the minute quantities of iodine which the sea water contains, to such an extent that it can be extracted from them with profit.

Iodine is obtained for the most part from seaweeds. On the coasts of Scotland, Ireland, and France the seaweeds which contain iodine are gathered, dried, and burned at a low heat. The organic portions are thus destroyed, and the ashes which contain the mineral constituents, including iodine in the form of iodide of potassium or of sodium, are treated with boiling water, and the solution thus obtained is evaporated. The iodides, being much more soluble than the other constituents of the ash, remain dissolved after most of the other salts have crystallized out, and they can be obtained in a comparatively pure condition by further evaporation. Iodine is set free from these iodides by adding to them some manganese dioxide and sulphuric acid, and gently heating the mixture.



Though solid at the ordinary temperature, iodine is easily vaporized, and the vapor obtained may be condensed in suitable vessels.

Exp. 57.—Place in a test tube a few small crystals of potassium iodide, add 2 g. of manganese dioxide and 2 cc. of concentrated sulphuric acid (H_2SO_4), and warm gently. Iodine will be set free in the

form of a violet vapor, and will condense on the upper portion of the tube in the form of minute crystals.

110. At the ordinary temperature, iodine is a soft, heavy, crystalline solid, of bluish black color and metallic luster. Its specific gravity is 4.6. It vaporizes rather freely at the ordinary temperature of the air, and the more rapidly when it is in a moist condition. Its odor is peculiar, somewhat resembling that of chlorine, but weaker, and easily distinguished from it. It is only slightly soluble in water, but dissolves readily in alcohol, to which it imparts a deep brown color.

The vapor of iodine is of a magnificent purple color, whence the name *iodine*, from a Greek word signifying "violet colored." This vapor is very heavy, nearly 9 times as heavy as air. Its specific gravity referred to hydrogen is 126.

Exp. 58. — Hold a dry test tube in the gas lamp by means of the wooden nippers, and warm it along its entire length, in so far as this is practicable. Drop into the hot tube a small fragment of iodine, and observe the vapor as it rises in the tube. If only a small portion of the tube were heated, the vapor would be deposited as solid iodine upon the cold part of its walls.

111. Solid iodine is never met with in the amorphous, shapeless state in which glass, resin, coal, and many other substances occur. No matter how obtained, its particles always exhibit a definite *crystalline* structure. If the iodine be melted, and then allowed to cool, or if it be converted into vapor, and this vapor be subsequently condensed, crystals will be formed in either case. Iodine has a characteristic strong taste. It colors the skin a yellowish brown, and, when applied externally as a counter irritant, it causes the reduction of some kinds of swellings, and excites the tissues to healthy action. It is a valued medicament; but, when swallowed in the solid state, it acts as an energetic corrosive poison.

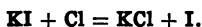
112. A singular property of iodine is its power of forming a blue compound with *starch*.

Exp. 59. — Prepare a quantity of thin starch paste by boiling 30 cc. of water in a porcelain dish, and stirring into it 0.5 g. of starch which has previously been reduced to the consistency of cream by rubbing it in a mortar with a few drops of water.

Pour 3 or 4 drops of the paste into 10 cc. of water in a test tube, and shake the mixture so that the paste may be equably diffused through the water; then add a drop of an aqueous solution of iodine, and observe the beautiful blue color which the solution assumes. If the solution be heated gently, the blue coloration will disappear; but it reappears when the liquid is allowed to cool.

Dip a strip of white paper in the starch paste, and suspend it, while still moist, in a large bottle, into the bottom of which two or three crystals of iodine have been thrown. As the vapor of iodine slowly diffuses through the air of the bottle, it will at last come in contact with the starch, and after some minutes the paper will be colored blue.

This reaction furnishes a very delicate test for iodine. By its means it has been proved that iodine, though nowhere very abundant, is very widely distributed in nature. This reaction is also made the basis of a test for chlorine. Strips of paper are smeared with starch paste into which potassium iodide in solution has been stirred. The paper is dried, and kept in stoppered bottles. When a strip of this paper is moistened and exposed to chlorine gas, the chlorine attacks the potassium iodide, potassium chloride is formed, and iodine is set free. The iodine thus set free manifests itself by imparting the characteristic blue color to the starch, —



Exp. 60. — Put in a test tube 1 g. of manganese dioxide. Pour upon it 1 cc. of concentrated hydrochloric acid, and warm gently. Now hold a piece of moistened iodo-starch paper over the tube and notice the result. If the iodo-starch paper is held too long in contact with the chlorine, the blue color due to the free iodine disappears, owing to oxidation taking place and iodic acid (HIO_3) being formed.

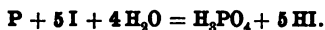
Bromine and chlorine are both capable of replacing iodine and setting it free from its compounds, as can be well illustrated by the following experiment.

Exp. 61. — Put a small quantity of a very dilute solution of potassium iodide in a test tube, add a few drops of carbon disulphide and a few drops of chlorine water, shake the tube, and allow it to stand for a few moments. Repeat the experiment, using bromine water instead of chlorine water. In both cases the carbon disulphide will dissolve the iodine which has been set free from the iodide of potassium, and assume a deep violet color.

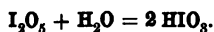
113. As has been already stated, iodine, in its chemical behavior, resembles chlorine and bromine, only its affinities are more feeble. It enters into combination with less energy than either of these elements, and is displaced by them from most of its combinations. Like them, it unites directly with the metals and with several other elements. It gradually corrodes organic tissues, and destroys coloring matters, though but slowly. Iodine and certain of its compounds are much used in medicine and in photography.

114. **Hydriodic acid (HI)** is a colorless gas of suffocating odor, very soluble in water. The aqueous solution has the general properties of hydrochloric acid. The gas is made up of equal volumes of hydrogen and iodine vapor. The proportions by weight are 1 part of hydrogen to 126 parts of iodine. The chemical effect of the small proportion of hydrogen contained in hydriodic acid is most remarkable. Only $\frac{1}{127}$, or less than 1 per cent, of hydriodic acid, is hydrogen; yet this very small proportional quantity of hydrogen is competent to impart to the new compound properties possessed by neither the iodine nor the hydrogen: the acid bears no resemblance to either of its constituents.

Hydrogen and iodine do not readily unite directly: a very high temperature is necessary to cause combination to take place. Even when indirect methods are resorted to, it is less easy to prepare hydriodic than hydrochloric or hydrobromic acid. The method adopted is like that used for the preparation of hydrobromic acid. It consists in treating phosphorus with iodine and water, —



115. **Iodic acid (HIO₃)** is analogous to chloric and bromic acids, but differs from them in being much more stable. It can be made by treating iodine with strong oxidizing agents. It is a crystallized solid, which, when heated to 170°, loses water and yields iodine pentoxide (I₂O₅), which may be regarded as the anhydride of the acid, just as N₂O₅ is the anhydride of nitric acid.



The *iodates* correspond in composition and general character to the bromates and chlorates, but are much more stable bodies,

ent of the uncrystallizable residue, called *bittern*, which remains after the sodium chloride has been crystallized out from the natural brines. At several saline springs this bittern contains so large a proportion of the bromide, that bromine can be profitably extracted from it. Most of the bromine of commerce is thus obtained. The method of preparation is to treat a mixture of a sodium bromide or potassium bromide and manganese dioxide with sulphuric acid.



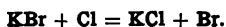
Exp. 54. — Mix half a gram of potassium bromide and a gram of manganese dioxide in a large test tube, and cover the mixture with dilute sulphuric acid. Bromine will be set free as a reddish brown gas, which will rapidly bleach a bit of moistened litmus paper. This experiment should be performed where there is a good draught, as should be all experiments with bromine, since its vapor is exceedingly irritating. Wounds produced when liquid bromine comes in contact with the skin are painful and dangerous.

105. At the ordinary temperature, bromine is a liquid of dark brown-red color, about three times as heavy as water, and highly poisonous. Its odor is irritating and disagreeable, whence the name *bromine*, derived from a Greek word signifying "a stench." It boils at about 60°, but is very volatile even at the ordinary temperature of the air.

Exp. 55. — By means of a small pipette, throw into a flask or bottle of 1 or 2 l. capacity 3 or 4 drops of bromine. Cover the bottle loosely, and leave it standing. In a short time it will be filled with a red vapor, which is bromine gas. This vapor is very heavy, more than 5 times as heavy as air, and rather more than 79 times heavier than hydrogen. Like chlorine, bromine is soluble in water, 1 part dissolving in about 33 parts of water. This aqueous solution is decomposed, like that of chlorine, on exposure to sunlight.

106. In its chemical behavior, as well as in many of its physical properties, bromine closely resembles chlorine, but it is liberated by chlorine from its compounds.

Exp. 56. — Make a solution of a few small crystals of potassium bromide in 5 cc. of water. Add a drop or two of chlorine water. Bromine will be set free, and will color the water.

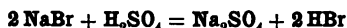


If, now, two drops of carbon disulphide (CS_2) be added, and the tube be shaken, the free bromine will be dissolved by the carbon disulphide, which will take on a deep reddish brown color.

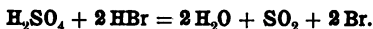
The affinity of bromine for hydrogen, though weaker than that of chlorine, is still powerful. When mixed, the two gases do not combine on mere exposure to sunlight, heat being necessary to bring about their union. Like chlorine, bromine is an energetic bleaching and disinfecting agent, the chemical action of the two elements being similar in kind, though somewhat different in degree. A lighted taper burns for an instant in bromine vapor, and is then extinguished.

If finely powdered metallic antimony be thrown into bromine, violent chemical action takes place. The metal burns as in chlorine, antimony bromide being formed. Similar action takes place in the case of many other substances with which bromine combines directly to form bromides.

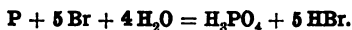
107. Hydrobromic Acid (HBr).—Like chlorine, bromine forms with hydrogen a compound in which equal volumes of the two elements (the bromine being in the state of vapor) are united without condensation. Hydrobromic acid is a colorless, irritating gas, readily soluble in water, forming a strongly acid solution which resembles hydrochloric acid in many respects in its chemical action. It might naturally be expected that this acid could be prepared by a reaction similar to that employed in the preparation of hydrochloric acid; viz., by treating a bromide with sulphuric acid. But strong sulphuric acid decomposes hydrobromic acid, which is less stable than hydrochloric acid; and, although the reaction



does take place, a further reaction, resulting in the decomposition of the hydrobromic acid, occurs:—



Hydrobromic acid is usually prepared by the action of bromine and phosphorus upon each other in the presence of water, the reaction being represented by the equation—



No oxides of bromine have as yet been isolated.

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Bromic acid (HBrO_3) is analogous to chloric acid (HClO_3). The *bromates* resemble the corresponding chlorates, and are prepared in a similar manner. No acids of bromine corresponding to chlorous or perchloric acid have as yet been obtained. Bromine and its compounds are used in the analytical laboratory, and in medicine and photography, as well as in the manufacture of certain dyestuffs obtainable from coal tar.

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Iodine is obtained for the most part from seaweeds. On the coasts of Scotland, Ireland, and France the seaweeds which contain iodine are gathered, dried, and burned at a low heat. The organic portions are thus destroyed, and the ashes which contain the mineral constituents, including iodine in the form of iodide of potassium or of sodium, are treated with boiling water, and the solution thus obtained is evaporated. The iodides, being much more soluble than the other constituents of the ash, remain dissolved after most of the other salts have crystallized out, and they can be obtained in a comparatively pure condition by further evaporation. Iodine is set free from these iodides by adding to them some manganese dioxide and sulphuric acid, and gently heating the mixture.



Though solid at the ordinary temperature, iodine is easily vaporized, and the vapor obtained may be condensed in suitable vessels.

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form of a violet vapor, and will condense on the upper portion of the tube in the form of minute crystals.

110. At the ordinary temperature, iodine is a soft, heavy, crystalline solid, of bluish black color and metallic luster. Its specific gravity is 4.6. It vaporizes rather freely at the ordinary temperature of the air, and the more rapidly when it is in a moist condition. Its odor is peculiar, somewhat resembling that of chlorine, but weaker, and easily distinguished from it. It is only slightly soluble in water, but dissolves readily in alcohol, to which it imparts a deep brown color.

The vapor of iodine is of a magnificent purple color, whence the name *iodine*, from a Greek word signifying "violet colored." This vapor is very heavy, nearly 9 times as heavy as air. Its specific gravity referred to hydrogen is 126.

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111. Solid iodine is never met with in the amorphous, shapeless state in which glass, resin, coal, and many other substances occur. No matter how obtained, its particles always exhibit a definite *crystalline* structure. If the iodine be melted, and then allowed to cool, or if it be converted into vapor, and this vapor be subsequently condensed, crystals will be formed in either case. Iodine has a characteristic strong taste. It colors the skin a yellowish brown, and, when applied externally as a counter irritant, it causes the reduction of some kinds of swellings, and excites the tissues to healthy action. It is a valued medicament; but, when swallowed in the solid state, it acts as an energetic corrosive poison.

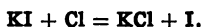
112. A singular property of iodine is its power of forming a blue compound with *starch*.

Exp. 59. — Prepare a quantity of thin starch paste by boiling 30 cc. of water in a porcelain dish, and stirring into it 0.5 g. of starch which has previously been reduced to the consistency of cream by rubbing it in a mortar with a few drops of water.

Pour 3 or 4 drops of the paste into 10 cc. of water in a test tube, and shake the mixture so that the paste may be equably diffused through the water; then add a drop of an aqueous solution of iodine, and observe the beautiful blue color which the solution assumes. If the solution be heated gently, the blue coloration will disappear; but it reappears when the liquid is allowed to cool.

Dip a strip of white paper in the starch paste, and suspend it, while still moist, in a large bottle, into the bottom of which two or three crystals of iodine have been thrown. As the vapor of iodine slowly diffuses through the air of the bottle, it will at last come in contact with the starch, and after some minutes the paper will be colored blue.

This reaction furnishes a very delicate test for iodine. By its means it has been proved that iodine, though nowhere very abundant, is very widely distributed in nature. This reaction is also made the basis of a test for chlorine. Strips of paper are smeared with starch paste into which potassium iodide in solution has been stirred. The paper is dried, and kept in stoppered bottles. When a strip of this paper is moistened and exposed to chlorine gas, the chlorine attacks the potassium iodide, potassium chloride is formed, and iodine is set free. The iodine thus set free manifests itself by imparting the characteristic blue color to the starch, —



Exp. 60. — Put in a test tube 1 g. of manganese dioxide. Pour upon it 1 cc. of concentrated hydrochloric acid, and warm gently. Now hold a piece of moistened iodo-starch paper over the tube and notice the result. If the iodo-starch paper is held too long in contact with the chlorine, the blue color due to the free iodine disappears, owing to oxidation taking place and iodic acid (HIO_3) being formed.

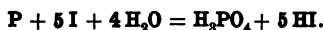
Bromine and chlorine are both capable of replacing iodine and setting it free from its compounds, as can be well illustrated by the following experiment.

Exp. 61. — Put a small quantity of a very dilute solution of potassium iodide in a test tube, add a few drops of carbon disulphide and a few drops of chlorine water, shake the tube, and allow it to stand for a few moments. Repeat the experiment, using bromine water instead of chlorine water. In both cases the carbon disulphide will dissolve the iodine which has been set free from the iodide of potassium, and assume a deep violet color.

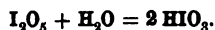
113. As has been already stated, iodine, in its chemical behavior, resembles chlorine and bromine, only its affinities are more feeble. It enters into combination with less energy than either of these elements, and is displaced by them from most of its combinations. Like them, it unites directly with the metals and with several other elements. It gradually corrodes organic tissues, and destroys coloring matters, though but slowly. Iodine and certain of its compounds are much used in medicine and in photography.

114. **Hydriodic acid (HI)** is a colorless gas of suffocating odor, very soluble in water. The aqueous solution has the general properties of hydrochloric acid. The gas is made up of equal volumes of hydrogen and iodine vapor. The proportions by weight are 1 part of hydrogen to 126 parts of iodine. The chemical effect of the small proportion of hydrogen contained in hydriodic acid is most remarkable. Only $\frac{1}{127}$, or less than 1 per cent, of hydriodic acid, is hydrogen; yet this very small proportional quantity of hydrogen is competent to impart to the new compound properties possessed by neither the iodine nor the hydrogen: the acid bears no resemblance to either of its constituents.

Hydrogen and iodine do not readily unite directly: a very high temperature is necessary to cause combination to take place. Even when indirect methods are resorted to, it is less easy to prepare hydriodic than hydrochloric or hydrobromic acid. The method adopted is like that used for the preparation of hydrobromic acid. It consists in treating phosphorus with iodine and water, —



115. **Iodic acid (HIO₃)** is analogous to chloric and bromic acids, but differs from them in being much more stable. It can be made by treating iodine with strong oxidizing agents. It is a crystallized solid, which, when heated to 170°, loses water and yields iodine pentoxide (I₂O₅), which may be regarded as the anhydride of the acid, just as N₂O₅ is the anhydride of nitric acid.



The *iodates* correspond in composition and general character to the *bromates* and *chlorates*, but are much more stable bodies,

Iodine pentoxide is a white solid, easily soluble in water. It does not undergo decomposition until heated to 300° . The compound of oxygen and iodine is thus much more stable than any of the oxides of chlorine, the affinity for oxygen of the members of the group increasing as that for hydrogen decreases.

Periodic acid (HIO_4) is analogous to perchloric acid: its salts are formed by the oxidation of iodates or by heating them.

116. Nitrogen Iodide. — Nitrogen forms, with chlorine, bromine, and iodine, a class of compounds which are very explosive. Nitrogen chloride is extremely dangerous, often exploding spontaneously without apparent cause. Nitrogen iodide is much less explosive, and may safely be prepared in very small quantities.

Exp. 62. — Place 0.25 g. of finely powdered iodine in a porcelain capsule, pour upon it enough concentrated ammonia water to somewhat more than cover the iodine, and allow the mixture to stand during 15 or 20 minutes. Collect in several small filters (Appendix, § 15) the insoluble dark brown powder which will be found at the bottom of the liquid. Wash well with cold water, and then remove the filters, together with their contents, from the funnels; pin them upon bits of board, and allow them to dry spontaneously. The powder is nitrogen iodide. As soon as it has become thoroughly dry, it will explode upon being rubbed, even with a feather, or jarred, as by the shutting of a door, or by a blow upon the wall or table.

117. The Halogen Group. — Fluorine, chlorine, bromine, and iodine constitute one of the most remarkable and best-defined natural groups of elements. Whether we regard the uncombined elements or their compounds, it is impossible not to be struck with the close analogies which subsist between them.

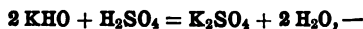
With hydrogen, all of these elements unite in the proportion of one volume to one volume, without condensation, to form acid compounds extremely soluble in water, and possessing throughout analogous properties. Moreover, with the exception of fluorine, each of them forms a powerful acid containing three atoms of oxygen, beside divers other compounds of obvious likeness. With nitrogen, they all form explosive compounds. With metals, the members of the group unite to form saline compounds (such as common salt, NaCl), whence the name *halogens* ("salt formers"). It will be noticed

that there is a marked family resemblance between the four halogen elements as regards their *physical* as well as their *chemical* characteristics; but, with all their properties, a distinct progression is observable from fluorine, through chlorine and bromine, to iodine. At the ordinary temperature, fluorine and chlorine are gases, bromine a liquid, and iodine a solid, though at temperatures not widely apart all but fluorine are known in the gaseous and liquid states.

The specific gravity of bromine vapor is greater than that of chlorine, and that of iodine greater than that of bromine. Fluorine gas is almost colorless, chlorine is a yellowish green gas, the vapor of bromine is reddish brown, and that of iodine violet. So with all their other properties, — fluorine will be at one end of the scale, iodine at the other, while chlorine and bromine invariably occupy intermediate positions.

The properties of the elements constituting this group illustrate a general principle; namely, that, among the members of a natural chemical group, *chemical energy* varies in the inverse direction of the *atomic weights*. Thus the atomic weight of fluorine is 19; that of chlorine is 35.2; that of bromine, 79.4; and that of iodine, 126: while the chemical energy of these elements follows the opposite order, fluorine being the most energetic, and iodine the least so. It will be seen on subsequent pages, that all the elements naturally fall into a few well-marked groups, and that the members of each of these groups resemble one another more or less closely as to their physical and chemical properties, which always vary in the order of the atomic weights.

118. **Halides.** — Originally the term *salt* (§§ 67, 68) was applied not only to sodium chloride, but to any saline substance which bore even a superficial resemblance to common salt; but, with the progress of knowledge, the meaning of the word has been greatly extended and modified. Nowadays the term *salt* as used by chemists does not necessarily imply the old idea of salinity, and there is even a disposition to restrict the word to bodies produced by the action of oxygen acids upon hydroxides of metals, — as when potassium hydroxide reacts with sulphuric acid to form the salt potassium sulphate, together with water,



and to apply the term *halide* to compounds of a halogen and a metallic element. Thus the compounds NaCl , KBr , and CaF_2 are halides. Vast numbers of halides have been described. Some of them unite with others to form double compounds which are analogous in several respects to the salts formed by the reaction of acids and bases that contain oxygen. For example, the mineral cryolite (§ 89) is a double fluoride of sodium and aluminum ($3\text{NaF} \cdot \text{AlF}_3$), and several double chlorides will be mentioned in subsequent chapters. It is to be observed that there is a close analogy between the simple halides and the corresponding hydroxides. Thus common salt (NaCl) is akin to sodium hydroxide (NaOH), in which the group of atoms known as hydroxyl (OH) plays a similar part to the atom of chlorine in sodium chloride. In the same sense, the formula of fluor spar (CaF_2) is related to that of calcium hydroxide ($\text{Ca}(\text{OH})_2$).

CHAPTER IX.

OZONE.

119. Beside ordinary oxygen, such as is found in the air and has been prepared in Exps. 3 and 4, §§ 9 and 12, another kind or form of this element is known to chemists. This new modification of oxygen has received a special name, *ozone*.

Several other elements, notably sulphur, phosphorus, and carbon, occur, as oxygen does, in very unlike states, or with very different attributes, while the fundamental chemical identity of the substance is preserved. The word *allotropism* is employed to express this capability of some of the elements: it is derived from Greek words signifying "of a different habit or character." This word serves merely to bring into one category a considerable number of conspicuous facts, of whose essential nature we have still much to learn. There is, of course, no virtue in the word itself to explain or account for the phenomena to which it refers (compare § 172).

120. Ozone is an exceedingly energetic chemical agent which resembles chlorine in some respects: it can therefore be advantageously studied in connection with the chlorine group.

It was long ago noticed, that, when an electrical machine was put in operation, a peculiar, pungent odor was developed.

More recently it has been observed that the same odor is manifested during the electrolysis of water (§ 27), and that this odor resembles that evolved by moistened phosphorus when exposed to the air. It has gradually been made out, that the odor in each of these cases is due to the presence of a peculiar modification of oxygen, called *ozone* from a Greek word signifying "to smell."

121. Ozone may be best prepared by certain electrical machines devised for the purpose; but the phosphorus method is simple and convenient.

Exp. 63. — In a clean bottle of 1 or 2 l. capacity place a piece of phosphorus 2 or 3 cm. long, the surface of which has been scraped clean (under water) with a knife; pour water into the bottle until the phosphorus is half covered; close the bottle with a loose stopper, and set it aside in a place where the temperature is 20° or 30°. In the course of 10 or 15 minutes a column of fog, due to the formation of some hydrogen dioxide, will be seen to rise from that portion of the phosphorus which projects above the water; the original garlic odor of the phosphorus will soon be lost; and the peculiar odor of ozone will gradually pervade the bottle. After one or two hours, the bottle will be found to contain an abundance of ozone for purposes of illustration.

The chemical changes which occur during this experiment are complicated. It will be enough to say of them, that the phosphorus unites with oxygen from the air in the bottle to form an oxide of phosphorus; that during this process of oxidation a portion of the oxygen in the bottle is changed into ozone; and that some of the ozone remains, even after several hours, diffused in the air of the bottle.

It must be distinctly understood that only a very minute quantity of ozone is obtained in the foregoing experiment; but ozone is a substance possessing great chemical power, and but little of it is needed in order to exhibit its characteristic properties.

122. Ozone is an irritating, poisonous gas, which at extremely low temperatures may be compressed to a dark blue liquid. Air which is highly charged with ozone is irrespirable, and produces effects on the human subject similar to those produced by chlorine. Its odor, which has been compared to that of weak chlorine, is so powerful that it can be recognized in air containing only one millionth part of the gas. Like

108. **Hypobromous acid** (HBrO) closely resembles the corresponding acid of chlorine (§ 101).

Bromic acid (HBrO_3) is analogous to chloric acid (HClO_3). The *bromates* resemble the corresponding chlorates, and are prepared in a similar manner. No acids of bromine corresponding to chlorous or perchloric acid have as yet been obtained. Bromine and its compounds are used in the analytical laboratory, and in medicine and photography, as well as in the manufacture of certain dyestuffs obtainable from coal tar.

IODINE (I).—ATOMIC WEIGHT, 126.

109. **Iodine**, in its chemical properties, bears a striking resemblance to bromine and to chlorine. Compounds of the element exist in sea water and in many saline and mineral springs. The proportion of iodine in sea water is exceeding small, being even smaller than that of bromine; but iodine is obtained more readily than bromine, for iodine is absorbed from sea water by various marine plants, which, during their growth, collect and concentrate the minute quantities of iodine which the sea water contains, to such an extent that it can be extracted from them with profit.

Iodine is obtained for the most part from seaweeds. On the coasts of Scotland, Ireland, and France the seaweeds which contain iodine are gathered, dried, and burned at a low heat. The organic portions are thus destroyed, and the ashes which contain the mineral constituents, including iodine in the form of iodide of potassium or of sodium, are treated with boiling water, and the solution thus obtained is evaporated. The iodides, being much more soluble than the other constituents of the ash, remain dissolved after most of the other salts have crystallized out, and they can be obtained in a comparatively pure condition by further evaporation. Iodine is set free from these iodides by adding to them some manganese dioxide and sulphuric acid, and gently heating the mixture.



Though solid at the ordinary temperature, iodine is easily vaporized, and the vapor obtained may be condensed in suitable vessels.

Exp. 57.—Place in a test tube a few small crystals of potassium iodide, add 2 g. of manganese dioxide and 2 cc. of concentrated sulphuric acid (H_2SO_4), and warm gently. Iodine will be set free in the

form of a violet vapor, and will condense on the upper portion of the tube in the form of minute crystals.

110. At the ordinary temperature, iodine is a soft, heavy, crystalline solid, of bluish black color and metallic luster. Its specific gravity is 4.6. It vaporizes rather freely at the ordinary temperature of the air, and the more rapidly when it is in a moist condition. Its odor is peculiar, somewhat resembling that of chlorine, but weaker, and easily distinguished from it. It is only slightly soluble in water, but dissolves readily in alcohol, to which it imparts a deep brown color.

The vapor of iodine is of a magnificent purple color, whence the name *iodine*, from a Greek word signifying "violet colored." This vapor is very heavy, nearly 9 times as heavy as air. Its specific gravity referred to hydrogen is 126.

Exp. 58. — Hold a dry test tube in the gas lamp by means of the wooden nippers, and warm it along its entire length, in so far as this is practicable. Drop into the hot tube a small fragment of iodine, and observe the vapor as it rises in the tube. If only a small portion of the tube were heated, the vapor would be deposited as solid iodine upon the cold part of its walls.

111. Solid iodine is never met with in the amorphous, shapeless state in which glass, resin, coal, and many other substances occur. No matter how obtained, its particles always exhibit a definite *crystalline* structure. If the iodine be melted, and then allowed to cool, or if it be converted into vapor, and this vapor be subsequently condensed, crystals will be formed in either case. Iodine has a characteristic strong taste. It colors the skin a yellowish brown, and, when applied externally as a counter irritant, it causes the reduction of some kinds of swellings, and excites the tissues to healthy action. It is a valued medicament; but, when swallowed in the solid state, it acts as an energetic corrosive poison.

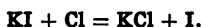
112. A singular property of iodine is its power of forming a blue compound with *starch*.

Exp. 59. — Prepare a quantity of thin starch paste by boiling 30 cc. of water in a porcelain dish, and stirring into it 0.5 g. of starch which has previously been reduced to the consistency of cream by rubbing it in a mortar with a few drops of water.

Pour 3 or 4 drops of the paste into 10 cc. of water in a test tube, and shake the mixture so that the paste may be equably diffused through the water; then add a drop of an aqueous solution of iodine, and observe the beautiful blue color which the solution assumes. If the solution be heated gently, the blue coloration will disappear; but it reappears when the liquid is allowed to cool.

Dip a strip of white paper in the starch paste, and suspend it, while still moist, in a large bottle, into the bottom of which two or three crystals of iodine have been thrown. As the vapor of iodine slowly diffuses through the air of the bottle, it will at last come in contact with the starch, and after some minutes the paper will be colored blue.

This reaction furnishes a very delicate test for iodine. By its means it has been proved that iodine, though nowhere very abundant, is very widely distributed in nature. This reaction is also made the basis of a test for chlorine. Strips of paper are smeared with starch paste into which potassium iodide in solution has been stirred. The paper is dried, and kept in stoppered bottles. When a strip of this paper is moistened and exposed to chlorine gas, the chlorine attacks the potassium iodide, potassium chloride is formed, and iodine is set free. The iodine thus set free manifests itself by imparting the characteristic blue color to the starch, —



Exp. 60. — Put in a test tube 1 g. of manganese dioxide. Pour upon it 1 cc. of concentrated hydrochloric acid, and warm gently. Now hold a piece of moistened iodo-starch paper over the tube and notice the result. If the iodo-starch paper is held too long in contact with the chlorine, the blue color due to the free iodine disappears, owing to oxidation taking place and iodic acid (HIO_3) being formed.

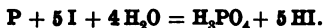
Bromine and chlorine are both capable of replacing iodine and setting it free from its compounds, as can be well illustrated by the following experiment.

Exp. 61. — Put a small quantity of a very dilute solution of potassium iodide in a test tube, add a few drops of carbon disulphide and a few drops of chlorine water, shake the tube, and allow it to stand for a few moments. Repeat the experiment, using bromine water instead of chlorine water. In both cases the carbon disulphide will dissolve the iodine which has been set free from the iodide of potassium, and assume a deep violet color.

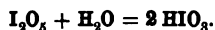
113. As has been already stated, iodine, in its chemical behavior, resembles chlorine and bromine, only its affinities are more feeble. It enters into combination with less energy than either of these elements, and is displaced by them from most of its combinations. Like them, it unites directly with the metals and with several other elements. It gradually corrodes organic tissues, and destroys coloring matters, though but slowly. Iodine and certain of its compounds are much used in medicine and in photography.

114. **Hydriodic acid (HI)** is a colorless gas of suffocating odor, very soluble in water. The aqueous solution has the general properties of hydrochloric acid. The gas is made up of equal volumes of hydrogen and iodine vapor. The proportions by weight are 1 part of hydrogen to 126 parts of iodine. The chemical effect of the small proportion of hydrogen contained in hydriodic acid is most remarkable. Only $\frac{1}{127}$, or less than 1 per cent, of hydriodic acid, is hydrogen; yet this very small proportional quantity of hydrogen is competent to impart to the new compound properties possessed by neither the iodine nor the hydrogen: the acid bears no resemblance to either of its constituents.

Hydrogen and iodine do not readily unite directly: a very high temperature is necessary to cause combination to take place. Even when indirect methods are resorted to, it is less easy to prepare hydriodic than hydrochloric or hydrobromic acid. The method adopted is like that used for the preparation of hydrobromic acid. It consists in treating phosphorus with iodine and water, —



115. **Iodic acid (HIO₃)** is analogous to chloric and bromic acids, but differs from them in being much more stable. It can be made by treating iodine with strong oxidizing agents. It is a crystallized solid, which, when heated to 170°, loses water and yields iodine pentoxide (I₂O₅), which may be regarded as the anhydride of the acid, just as N₂O₅ is the anhydride of nitric acid.



The *iodates* correspond in composition and general character to the bromates and chlorates, but are much more stable bodies,

Iodine pentoxide is a white solid, easily soluble in water. It does not undergo decomposition until heated to 300° . The compound of oxygen and iodine is thus much more stable than any of the oxides of chlorine, the affinity for oxygen of the members of the group increasing as that for hydrogen decreases.

Periodic acid (HIO_4) is analogous to perchloric acid: its salts are formed by the oxidation of iodates or by heating them.

116. Nitrogen Iodide. — Nitrogen forms, with chlorine, bromine, and iodine, a class of compounds which are very explosive. Nitrogen chloride is extremely dangerous, often exploding spontaneously without apparent cause. Nitrogen iodide is much less explosive, and may safely be prepared in very small quantities.

Exp. 62. — Place 0.25 g. of finely powdered iodine in a porcelain capsule, pour upon it enough concentrated ammonia water to somewhat more than cover the iodine, and allow the mixture to stand during 15 or 20 minutes. Collect in several small filters (Appendix, § 15) the insoluble dark brown powder which will be found at the bottom of the liquid. Wash well with cold water, and then remove the filters, together with their contents, from the funnels; pin them upon bits of board, and allow them to dry spontaneously. The powder is nitrogen iodide. As soon as it has become thoroughly dry, it will explode upon being rubbed, even with a feather, or jarred, as by the shutting of a door, or by a blow upon the wall or table.

117. The Halogen Group. — Fluorine, chlorine, bromine, and iodine constitute one of the most remarkable and best-defined natural groups of elements. Whether we regard the uncombined elements or their compounds, it is impossible not to be struck with the close analogies which subsist between them.

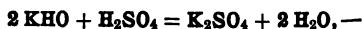
With hydrogen, all of these elements unite in the proportion of one volume to one volume, without condensation, to form acid compounds extremely soluble in water, and possessing throughout analogous properties. Moreover, with the exception of fluorine, each of them forms a powerful acid containing three atoms of oxygen, beside divers other compounds of obvious likeness. With nitrogen, they all form explosive compounds. With metals, the members of the group unite to form saline compounds (such as common salt, NaCl), whence the name *halogens* ("salt formers"). It will be noticed

that there is a marked family resemblance between the four halogen elements as regards their *physical* as well as their *chemical* characteristics; but, with all their properties, a distinct progression is observable from fluorine, through chlorine and bromine, to iodine. At the ordinary temperature, fluorine and chlorine are gases, bromine a liquid, and iodine a solid, though at temperatures not widely apart all but fluorine are known in the gaseous and liquid states.

The specific gravity of bromine vapor is greater than that of chlorine, and that of iodine greater than that of bromine. Fluorine gas is almost colorless, chlorine is a yellowish green gas, the vapor of bromine is reddish brown, and that of iodine violet. So with all their other properties, — fluorine will be at one end of the scale, iodine at the other, while chlorine and bromine invariably occupy intermediate positions.

The properties of the elements constituting this group illustrate a general principle; namely, that, among the members of a natural chemical group, *chemical energy* varies in the inverse direction of the *atomic weights*. Thus the atomic weight of fluorine is 19; that of chlorine is 35.2; that of bromine, 79.4; and that of iodine, 126: while the chemical energy of these elements follows the opposite order, fluorine being the most energetic, and iodine the least so. It will be seen on subsequent pages, that all the elements naturally fall into a few well-marked groups, and that the members of each of these groups resemble one another more or less closely as to their physical and chemical properties, which always vary in the order of the atomic weights.

118. **Halides.** — Originally the term *salt* (§§ 67, 68) was applied not only to sodium chloride, but to any saline substance which bore even a superficial resemblance to common salt; but, with the progress of knowledge, the meaning of the word has been greatly extended and modified. Nowadays the term *salt* as used by chemists does not necessarily imply the old idea of salinity, and there is even a disposition to restrict the word to bodies produced by the action of oxygen acids upon hydroxides of metals, — as when potassium hydroxide reacts with sulphuric acid to form the salt potassium sulphate, together with water,



and to apply the term *halide* to compounds of a halogen and a metallic element. Thus the compounds NaCl , KBr , and CaF_2 are halides. Vast numbers of halides have been described. Some of them unite with others to form double compounds which are analogous in several respects to the salts formed by the reaction of acids and bases that contain oxygen. For example, the mineral cryolite (§ 89) is a double fluoride of sodium and aluminum ($3\text{NaF} \cdot \text{AlF}_3$), and several double chlorides will be mentioned in subsequent chapters. It is to be observed that there is a close analogy between the simple halides and the corresponding hydroxides. Thus common salt (NaCl) is akin to sodium hydroxide (NaOH), in which the group of atoms known as hydroxyl (OH) plays a similar part to the atom of chlorine in sodium chloride. In the same sense, the formula of fluor spar (CaF_2) is related to that of calcium hydroxide ($\text{Ca}(\text{OH})_2$).

CHAPTER IX.

OZONE.

119. Beside ordinary oxygen, such as is found in the air and has been prepared in Exps. 3 and 4, §§ 9 and 12, another kind or form of this element is known to chemists. This new modification of oxygen has received a special name, *ozone*.

Several other elements, notably sulphur, phosphorus, and carbon, occur, as oxygen does, in very unlike states, or with very different attributes, while the fundamental chemical identity of the substance is preserved. The word *allotropism* is employed to express this capability of some of the elements: it is derived from Greek words signifying "of a different habit or character." This word serves merely to bring into one category a considerable number of conspicuous facts, of whose essential nature we have still much to learn. There is, of course, no virtue in the word itself to explain or account for the phenomena to which it refers (compare § 172).

120. Ozone is an exceedingly energetic chemical agent which resembles chlorine in some respects: it can therefore be advantageously studied in connection with the chlorine group.

It was long ago noticed, that, when an electrical machine was put in operation, a peculiar, pungent odor was developed.

More recently it has been observed that the same odor is manifested during the electrolysis of water (§ 27), and that this odor resembles that evolved by moistened phosphorus when exposed to the air. It has gradually been made out, that the odor in each of these cases is due to the presence of a peculiar modification of oxygen, called *ozone* from a Greek word signifying "to smell."

121. Ozone may be best prepared by certain electrical machines devised for the purpose; but the phosphorus method is simple and convenient.

Exp. 63. — In a clean bottle of 1 or 2 l. capacity place a piece of phosphorus 2 or 3 cm. long, the surface of which has been scraped clean (under water) with a knife; pour water into the bottle until the phosphorus is half covered; close the bottle with a loose stopper, and set it aside in a place where the temperature is 20° or 30°. In the course of 10 or 15 minutes a column of fog, due to the formation of some hydrogen dioxide, will be seen to rise from that portion of the phosphorus which projects above the water; the original garlic odor of the phosphorus will soon be lost; and the peculiar odor of ozone will gradually pervade the bottle. After one or two hours, the bottle will be found to contain an abundance of ozone for purposes of illustration.

The chemical changes which occur during this experiment are complicated. It will be enough to say of them, that the phosphorus unites with oxygen from the air in the bottle to form an oxide of phosphorus; that during this process of oxidation a portion of the oxygen in the bottle is changed into ozone; and that some of the ozone remains, even after several hours, diffused in the air of the bottle.

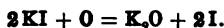
It must be distinctly understood that only a very minute quantity of ozone is obtained in the foregoing experiment; but ozone is a substance possessing great chemical power, and but little of it is needed in order to exhibit its characteristic properties.

122. Ozone is an irritating, poisonous gas, which at extremely low temperatures may be compressed to a dark blue liquid. Air which is highly charged with ozone is irrespirable, and produces effects on the human subject similar to those produced by chlorine. Its odor, which has been compared to that of weak chlorine, is so powerful that it can be recognized in air containing only one millionth part of the gas. Like

chlorine, ozone bleaches and destroys vegetable coloring matters, and is a powerful disinfectant. Like chlorine, it instantly decomposes the iodides of the metals: upon this property is based a ready method of testing for its presence.

Exp. 64. — Into the bottle of ozonized air (Exp. 63, § 121) thrust a moistened slip of test paper saturated with starch and iodide of potassium, prepared as described in § 112. The paper will instantly acquire a deep blue tint.

As in the case where the test paper is employed for detecting chlorine (§ 112), so here, the reaction depends upon the displacement of the chemically feeble iodine by the more powerful ozone, and it would seem at first sight as if the reaction might be written, —



The ozone here acts as oxygen, in one sense: at all events, the potassium oxide formed is not to be distinguished from potassium oxide prepared with common oxygen; but this in no wise contradicts the fact that ozone is an extraordinarily active and energetic variety of oxygen, inasmuch as common oxygen will not effect this decomposition. Its chemical action is, however, very different from that of oxygen. While oxygen is, at ordinary temperatures, comparatively inactive, ozone is exceedingly active, oxidizing nearly all the metals, beside producing a variety of other changes which are not produced by oxygen at the ordinary temperature.

123. The great difference between ordinary oxygen and the allotropic modification, ozone, is generally explained by supposing, that, while the molecules of oxygen and the molecules of ozone are both made up of oxygen atoms, the former contains two atoms in each molecule (§ 170), while the latter contains three atoms. This idea is strengthened by the fact that when oxygen is converted into ozone a condensation takes place, and when the ozone is reconverted into ordinary oxygen there is an expansion to the original bulk. Other observed facts lead to the same conclusion; and it is known that only the third atom of oxygen is removed when ozone acts upon potassium iodide, as is expressed by the equation —



As was just now said, there are several other elements which occur in allotropic forms, and it is quite probable that the same explanation may hold good in these cases; viz., that the differences are due to a difference in the molecular constitution.

124. The oxidizing power of ozone is intense. When moisture is present, it oxidizes all the metals excepting gold, platinum, and the platinum metals. Even silver is oxidized by it at the ordinary temperature, and becomes covered with a brown coating of an oxide of silver. In like manner most organic substances are quickly oxidized by ozone. When substances such as sawdust, garden mold, powdered charcoal, milk, or flesh, are thrown into a bottle of ozonized air, the odor of ozone instantly disappears.

By virtue of this strong oxidizing power, ozone is of great importance as a *disinfecting agent*. It destroys instantly a multitude of offensive gases, such as arise from decaying animal and vegetable matter, and has been frequently recommended as a substance well fitted for the purification of sick rooms and hospital wards.

125. A minute proportion of ozone seems to exist in normal atmospheric air: it is especially abundant after a thunderstorm. It is seldom found in the air of thickly inhabited localities. At temperatures above 100°, ozone is converted into ordinary oxygen.

CHAPTER X.

SULPHUR, SELENIUM, AND TELLURIUM.

SULPHUR (S).—ATOMIC WEIGHT, 32.

126. Sulphur occurs somewhat abundantly in nature both in the free state and in combination with other elements. Many ores of metals, for example, are sulphur compounds. It is a component of several abundant salts, such as the sulphates of calcium, barium, and sodium, and occurs in small proportion in many animal and vegetable substances. Free sulphur is found chiefly in volcanic districts. Generally it occurs mixed with earthy matters; but it often forms distinct veins, and is sometimes found in the shape of well-defined crystals of considerable size. At the present time about nine tenths of the sulphur of commerce comes from Sicily.

Native sulphur is usually subjected to a rough purification at the place of its occurrence. This purification is sometimes effected by distilling the volcanic earth in retorts or jars of earthenware; or, if the earth be very rich in sulphur, it is simply heated in large kettles, and the melted sulphur dipped off from above, while the earthy impurities settle to the bottom of the kettle. Poor earths are sometimes piled up in large kilns, and set on fire, a portion of the sulphur in burning furnishing the heat by which the rest of the sulphur is melted. The melted sulphur flows out from the mass, and is collected in receivers. A recent method of preparation is to melt it under water in a boiler by forcing in steam until the temperature of the water is raised above the melting point of sulphur. The molten sulphur is run off through a stopcock in the side of the boiler, and, when cold, a fresh charge of impure sulphur is introduced, and the operation repeated. As the crude sulphur comes to us, it is in irregular lumps of a dirty light yellow color, and is largely employed for manufacturing purposes. It is purified by being distilled from iron retorts into large chambers constructed of masonry, in which it is deposited either in the form of a light powder, known as *flowers of sulphur*, or in the liquid state, according to the temperature of the chambers. This liquid sulphur is drawn off into wooden molds, and thus cast into the sticks familiarly known as roll brimstone.

127. At the ordinary temperature of the air, sulphur is a brittle solid of a peculiar light yellow color. It has neither taste nor smell, excepting that when rubbed it exhales a faint and peculiar odor. Most of the odors which in everyday life are referred to sulphur are really the odors of various compounds of sulphur, and are not evolved by the element itself. The symbol of sulphur is S. It is noteworthy that its atomic weight, 32, is twice as great as the atomic weight of oxygen.

128. Sulphur behaves in a very remarkable manner on being heated. When melted at the lowest possible temperature, 110° to 115°, it forms a limpid liquid of a light yellow color; but, if this liquid be heated more strongly, it begins to become viscid and dark colored at about 150°; and at 170° to 200° it is almost black, and at the same time so thick and tenacious that it cannot be poured from the vessel which holds it, even if the vessel be inverted; at 330° to 340° it regains its fluidity in part, though the liquid is still dark colored; and finally, at about 440°, it begins to boil, and is converted into an amber-colored vapor.

129. If melted sulphur in the viscid state, or, better, that which has regained its mobility, be suddenly cooled, a semi-solid modification of sulphur, remarkably different from the ordinary form, will be obtained.

Exp. 65. — Place in a test tube of about 30 cc. capacity 15 to 20 g. of coarsely powdered sulphur; melt the sulphur slowly over the gas lamp, and continue to heat it until it begins to boil, noting, meanwhile, the changes which the sulphur undergoes, as described in § 128. Finally pour the hot sulphur, in a fine stream, into a large dish full of cold water. There will be obtained a soft, elastic, reddish brown mass, which can be kneaded and molded like wax, and drawn out into threads like caoutchouc.



Fig. 24.

This soft or amorphous sulphur cannot be preserved for any great length of time: it slowly hardens, and changes into ordinary brittle yellow sulphur.

130. Sulphur may readily be obtained in the form of crystals.

Exp. 66. — In a small beaker or Hessian crucible slowly heat 50 to 60 g. of sulphur until it has entirely melted. Remove the vessel from the lamp, and allow it to cool slowly until about a quarter part of the sulphur has solidified; then pour off into a basin of water that portion of the sulphur which is still liquid, breaking through, for this purpose, the crust at the top of the liquid, if any such has formed. The interior of the vessel will be found to be lined with transparent crystals.

Exp. 67. — In a test tube melt enough sulphur to fill one quarter of the tube; place the tube in such a position that its contents may cool slowly and quietly, and then watch the formation of crystals as they shoot out from the comparatively cold walls of the tube towards the center of the liquid.

Experiment 66 represents one general method of obtaining crystals. Crystals of many of the metals (lead and bismuth, for example) can be obtained in a similar manner: it is only necessary to perform the operation in a crucible of some refractory material, placed in a furnace.

Experiment 67, beside illustrating the manner in which crystals form, teaches us something of the physical structure of solid bodies. The solid mass of sulphur which is left in the test tube, when it has become cold, is evidently nothing more than a compact bundle of interlaced crystals: it possesses what is called a *crystalline structure*. This crystalline structure is apt to render a body brittle. Substances which possess it are liable to break with the grain, or to split in certain directions determined by the shape of the crystals, and called lines of *cleavage*. A stick of roll brimstone, for example, may be readily broken or cut across, but not so easily in the direction of its length.

131. Another easy way to crystallize sulphur is by the method of solution and evaporation, such as was employed in the preparation of potassium nitrate (Exp. 37, § 68). Sulphur is not soluble in water, but it dissolves readily in a liquid compound of sulphur and carbon, known as carbon disulphide, which, being readily volatile, quickly escapes, on exposure to the air, and so deposits the sulphur. The crystals thus obtained differ in shape from those obtained by the method of fusion.

Exp. 68.—Place in a test tube a small teaspoonful of flowers of sulphur; pour upon the sulphur 10 or 12 cc. of carbon disulphide; close the tube with a cork, and allow the mixture to stand during half an hour, shaking it occasionally. Decant the clear liquid from the sulphur which still remains undissolved, and pour it into a small porcelain dish, which place out of doors or in a draught of air, until the carbon disulphide has evaporated. Crystals of sulphur will then be found at the bottom of the dish. It is to be remembered that only a part of the sulphur taken is dissolved, for there is contained in flowers of sulphur a form of sulphur which is insoluble in carbon disulphide.

132. Although thousands of crystals of unlike shapes occur in nature or have been produced by art, it has been found possible to refer them all to six general classes of forms, called *systems of crystallization*.

In defining crystals thus in classes, certain axes or directions of growth are assumed to exist in the crystal, and its bounding surfaces have certain definite relations as regards their position in respect to these axes. As a rule, crystals are so constructed that every face, edge, or angle situated at one side is represented by a similar face, edge, or angle situated at the other side, and, if we imagine straight lines to be drawn from certain points on the one side to similar points upon the

other, they will intersect at the center. These lines are called the *axes*. The bounding planes of the crystals lie symmetrically around the *axes*, and the length and relative position of the *axes* determine the relative position of the surfaces of the crystal: they may be regarded as a kind of skeleton or framework upon or about which the crystal is constructed. The following are the six systems of crystallization:—

I. **Monometric or Regular System** (Fig. 25).—Three equal axes intersecting each other at right angles. The cube, regular octahedron, rhombic dodecahedron, and other perfectly symmetrical forms, belong to this system.

II. **Dimetric or Quadratic System** (Fig. 26).—Three axes intersecting each other at right angles; one axis longer or shorter than the other two, which are equal. The right square prism and octahedron with a square base belong to this system.

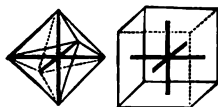


Fig. 25.

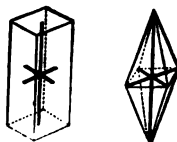


Fig. 26.

III. **Trimetric or Rhombic System** (Fig. 27).—Three axes intersecting each other at right angles, no two of them being of equal length. This system includes the right rectangular prism, the right rhombic prism, and corresponding octahedrons.

IV. **Monoclinic System** (Fig. 28).—Three unequal axes, one the vertical at right angles to one of the other two, which are called lateral, but obliquely inclined to the other axis. The two lateral axes intersect each other at right angles. The oblique rectangular prism, oblique rhombic prism, and corresponding octahedral forms, belong to this system.

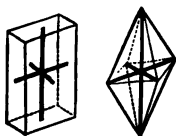


Fig. 27.

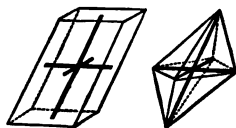


Fig. 28.

V. **Triclinic System** (Fig. 29).—Three unequal axes, all intersecting each other at oblique angles. The doubly oblique prism and doubly oblique octahedron are of this system.

VI. Hexagonal System (Fig. 30).—Four axes, —three lateral axes lying in one plane, of equal length, and intersecting each other at angles of 60° ; and a fourth or vertical axis, either longer or shorter than the other three, and crossing them at right angles. This system includes the hexagonal prism, hexagonal pyramid, and the rhombohedron.

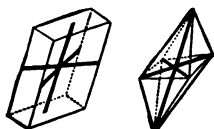


Fig. 29.

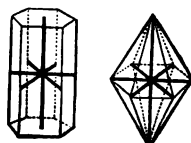


Fig. 30.

183. The variety of possible forms under these systems of crystallization is unlimited. Thus, when the axes are unequal, the inequality may be great or small, and in oblique systems the inclinations of the axes may vary indefinitely. But, no matter how complex the form of a crystal may be, the complication will be found to be caused by the combination of simple forms of the particular system to which the crystal belongs, not at all to any commingling of forms from other systems. It may be said in general terms that the crystalline form of any substance is a constant fundamental peculiarity of that substance as characteristic as its chemical composition, its specific gravity, or its boiling point. All of these attributes depend upon natural laws; i.e., upon forces which control the very existence of the substance. It is noticeable that substances which crystallize in the same system resemble one another as to their conductivity for heat and in respect to their optical properties. It is true of almost all chemical substances which can be obtained in crystals, that, while the individual crystals may vary somewhat in form, all the forms in which the substance occurs are such as may be referred to one and the same system. In the case of sulphur, however, we meet with an exception to this rule. The crystals obtained by the method of fusion are oblique rhombic prisms, and belong to the fourth system; while those obtained by the method of solution are rhombic octahedrons belonging to the third system. There are other substances beside sulphur which present this same phenomenon. Substances which are thus capable of assuming crystalline forms belonging to two different systems are said to be *dimorphous* ("two-formed").

The two varieties of sulphur differ considerably in various physical properties. One variety may, however, be converted into the other; and their chemical composition is identical. Each is sulphur, and nothing more. The amorphous soft sulphur obtained in Exp. 65, § 129, may be regarded as a third modification of sulphur. Thus it

appears that sulphur, like oxygen, is capable of assuming different allotropic states.

Crystals of sulphur of large size and great beauty occur in nature, and are supposed to have been formed by sublimation; i.e., the sulphur has been converted into vapor, and the vapor cooled very slowly. The method is hardly practicable in the laboratory, although crystals have been formed artificially in this way.

134. Sulphur is less active, chemically speaking, than the elements of the halogen group. It unites directly, though not readily, with hydrogen, and may be made to combine with nearly all the nonmetallic elements. It unites energetically with most metallic elements, forming compounds called *sulphides*, which generally have the same atomic composition as the corresponding oxide. Such union is in many cases attended with evolution of light and heat.

This fact has already been illustrated in the case of copper by Exp. 1, § 2. The product of the reaction was copper sulphide.

Exp. 69.— Mix intimately 4 g. of flowers of sulphur and 7 g. of the finest iron filings. Place the mixture in an ignition tube 10 to 12 cm. long, and heat the lower end of the tube over the gas lamp. In a short time the mass will begin to glow, as the sulphur and iron enter into chemical combination; and this ignition will, of itself, pass through the entire length of the tube, even if the lamp be withdrawn. The final product of the reaction is iron sulphide.

135. Sulphur unites readily with oxygen at a comparatively low temperature. When heated in the air, it takes fire at about 250° , and burns with a peculiar blue light. The irritating, suffocating gas produced will be shortly described under the name of *sulphur dioxide*.

The use of sulphur on ordinary matches depends on the low temperature at which it takes fire. Being ignited by the burning phosphorus, it burns until the less readily combustible wood is set on fire. Large quantities of sulphur are used in the arts. It is used in the manufacture of gunpowder, of sulphuric acid, and of fireworks; in vulcanizing caoutchouc; and as a means of bleaching wool and straw. Many of the sulphides are of considerable practical importance.

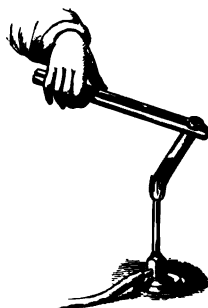


Fig. 31.

136. **Hydrogen sulphide (H_2S)**, or **sulphuretted hydrogen**, as it is often called, is a colorless gas which smells like rotten eggs. It may be conveniently prepared by treating iron sulphide with dilute hydrochloric acid.

Exp. 70. — In a gas bottle (Fig. 32) put 10 or 12 g. of iron sulphide (Exp. 69, § 134); replace the cork in the bottle and introduce the gas



Fig. 32.

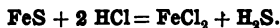
delivery tube into another small bottle containing cold water, letting it dip 5 or 6 cm. beneath the surface of the water. Through the thistle tube pour water enough into the gas bottle to seal the lower extremity of this tube; then add, through the thistle tube as before, 2 or 3 teaspoonfuls of strong hydrochloric acid, and observe that bubbles of gas soon begin to pass through the water in the absorption bottle.

Hydrogen sulphide is soluble in water to a considerable extent, and is consequently taken up by the water in the absorption bottle. The solution thus obtained, known as *sulphuretted hydrogen water*, is much employed as a reagent in chemical laboratories.

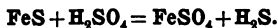
When the disengagement of gas slackens, a new portion of hydrochloric acid may be added through the thistle tube, and this process continued until the water in the absorption bottle smells strongly of the gas.

This experiment should be performed out of doors, or in a draught of air so arranged that those portions of the gas which escape solution shall be carried away from the operator.

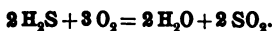
The reaction which takes place may be represented as follows:—



Sulphuric acid may perfectly well be substituted for the hydrochloric, in which case the reaction is—



137. Hydrogen sulphide is readily inflammable. It burns with a blue flame, producing water and sulphur dioxide:—



Exp. 71. — To the delivery tube of the gas bottle employed in generating hydrogen sulphide, attach a drying tube containing fragments of calcium chloride, and with the tube connect a piece of No. 6 glass tubing drawn out to a fine point. When the apparatus is full of the gas, apply a match to the end of the tube. The gas will take fire, and burn with a blue flame. If a dry bottle be held over the flame, the walls will become coated with moisture, which will have an acid reaction and will redden blue litmus paper.

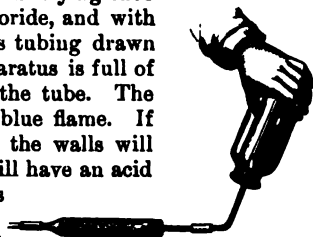
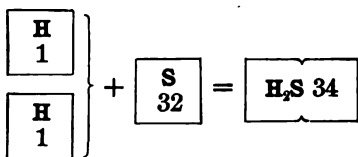


Fig. 33.

The jet of hydrogen sulphide should not be lighted until all the air is expelled from the apparatus, as this gas forms an explosive mixture with air.

138. Hydrogen sulphide is readily decomposed by heat, as may be shown by passing a current of the gas through a glass tube, heated for a portion of its length. The gas will be separated into hydrogen and sulphur: the latter will be deposited on the cold portion of the tube.

Analysis has proved that the composition of hydrogen sulphide, both by volume and by weight, may be expressed by the following diagram, in which the symbol S represents a unit volume of sulphur in the state of vapor: —

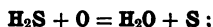


The product is similar, in respect to volumetric composition, to water vapor or dry steam.

139. Hydrogen sulphide is very poisonous. When respired in the pure state, it quickly proves fatal; and it is very deleterious, even though largely diluted with atmospheric air. Nausea and headache are often produced when an atmosphere even slightly contaminated with it is breathed for any length of time. It is therefore best, when experimenting with it, to operate where there is a free circulation of air.

The gas exists as a natural constituent of some mineral waters, which are thence called sulphurous, such as the Virginia Sulphur Springs, and the mineral springs at Sharon, N.Y. It is also found in the air and water of foul sewers, and where animal matter is undergoing putrefaction.

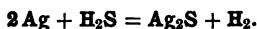
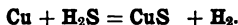
140. Water dissolves about three times its own volume of hydrogen sulphide at ordinary temperatures. This solution (Exp. 70, § 136) is transparent and colorless when freshly prepared, but when kept, it gradually becomes turbid through deposition of sulphur. Oxygen from the air unites with the hydrogen and sets free sulphur,



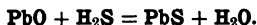
so that after a time the solution may no longer contain any of the gas. The moist gas and its aqueous solution have a slight acid reaction upon litmus.

141. When moist hydrogen sulphide comes in contact with certain of the metals, it is decomposed.

Exp. 72. — Place a drop of sulphuretted hydrogen water (Exp. 70, § 136) upon a bright piece of copper, lead, or silver. The metal will quickly become black. The sulphur of the hydrogen sulphide unites with the metal to form a sulphide of the metal, while the hydrogen escapes, or we may say that the metal *replaces* the hydrogen in the hydrogen sulphide.



Exp. 73. — Place in a test tube a little litharge (lead monoxide); pour upon it a teaspoonful of hydrogen sulphide solution. The brown litharge at once becomes black. Lead sulphide is formed, and water is set free, —

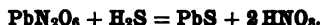


Similar reactions take place on treating many other metallic oxides with hydrogen sulphide.

From a solution of any compound of these metals, hydrogen sulphide will throw down the sulphide of the metal.

Exp. 74. — Dissolve a small crystal of lead nitrate in a test tube half full of water, and to this solution add a few drops of the sulphu-

retted hydrogen water. Lead sulphide is thrown down as a black precipitate, and nitric acid is set free:—



142. Since the sulphides of many elements are, like those of lead, copper, and silver, insoluble in water and dilute acids, hydrogen sulphide will precipitate them from solutions of their salts. Many of these precipitates are black, like that of lead; but sulphide of antimony is orange, sulphide of cadmium yellow, and zinc sulphide is white. The precipitates thus obtained often serve for the detection and characterization of the corresponding elements.

Exp. 75.— Take 20 cc. of a solution of each of the following substances: copper sulphate (CuSO_4), antimony chloride (SbCl_3), cadmium chloride (CdCl_2), and zinc sulphate (ZnSO_4); place the solutions in separate test tubes, and pass hydrogen sulphide through each of the solutions in turn.

A common method of detecting the presence of hydrogen sulphide depends upon the decomposition of lead acetate, lead sulphide being formed.

Exp. 76.— Moisten a piece of filter paper with a solution of lead acetate, and expose it to hydrogen sulphide from any source. The paper will immediately be blackened through the formation of lead sulphide, which often exhibits a peculiar lustrous appearance.

On account of its power of precipitating various metallic sulphides, hydrogen sulphide is much used in the analytical laboratory as a reagent.

143. Hydrogen sulphide is comparatively unstable, and may readily be decomposed in a variety of ways. When simply heated, it is decomposed into its elements, as has been seen already. All substances which readily give up oxygen decompose it, the oxygen uniting with the hydrogen to form water, while sulphur is set free. Chlorine, bromine, and iodine vapor instantly decompose it, uniting with its hydrogen to form the halogen acids, and setting sulphur free. It is thus seen to be a much less stable compound than the corresponding hydrogen oxide, water.

144. The chemical action of hydrogen sulphide shows that it belongs to the class of bodies called acids (§ 67). Its action on oxides (as in Exp. 73, § 141) is similar to the action of acids upon basic oxides, a sulphide and water being formed. The sulphides may thus be regarded as derived from hydrogen sulphide by the replacement of its hydrogen atoms. There is a class of bodies which can be regarded as derived

from hydrogen sulphide by the replacement of but one of its atoms of hydrogen by metallic atoms. They are known as the *hydrosulphides* or *sulphydrates*. For example, **KSH** (potassium hydrosulphide) and **NaSH** (sodium hydrosulphide) may be regarded as bearing the same relation to hydrogen sulphide that their hydroxides bear to water. On account of the fact that hydrogen sulphide forms salts in the same general way as acids, it is sometimes called *sulphydric acid*.

A compound of sulphur and hydrogen (hydrogen disulphide) analogous to hydrogen dioxide is known. Its composition may be represented by the formula H_2S_2 .

145. Sulphur and Oxygen.—Of the compounds of sulphur and oxygen, the most important are *sulphur dioxide* or *sulphurous oxide*, and *sulphur trioxide* or *sulphuric oxide*.

146. Sulphur dioxide (SO_2), commonly called *sulphurous acid*, is produced whenever sulphur is burned in air or in oxygen gas.

Exp. 77.—Light a piece of sulphur in a deflagrating spoon, and suspend the latter in a half-liter bottle full of air. On examining the contents of the bottle, after the sulphur has ceased to burn, there will be found an irritating, suffocating gas having the peculiar odor which is familiar as that of a burning match. The bottle is now full of sulphurous oxide mixed with the nitrogen originally present in the air.



Fig. 34.

An easier method of preparing pure sulphur dioxide is by depriving common sulphuric acid of part of its oxygen. This result can be effected by a variety of reducing or deoxidizing agents. For example, when concentrated sulphuric acid is heated with metallic copper, there is formed a sulphate of the metal, water, and sulphurous acid:—



Certain other metals, such as mercury, for example, can be employed instead of copper, the reaction being similar.

147. Sulphur dioxide is a transparent and colorless gas. It is irrespirable and suffocating, and when mixed with air, even in small proportion, occasions violent coughing. It is not inflammable, but, on the contrary, it stops combustion; nor does it readily give up its oxygen

The flame of a candle is immediately extinguished on being immersed in the gas, just as it is by nitrogen. A useful application of this property of sulphur dioxide is in extinguishing burning chimneys. A handful of fragments of sulphur being thrown into the fire, and the openings of the fireplace closed in such manner that little or no air shall enter the chimney, excepting that which passes through the fire, the chimney will quickly become filled with an atmosphere of sulphurous gas mixed with nitrogen from the air employed in burning the sulphur, and the burning soot upon the walls of the chimney will be extinguished.

It is, of course, essential that the chimney should then be closed at the top, so that air may be excluded, and the chimney kept full of the fire-extinguishing atmosphere until its walls shall have cooled to below the kindling temperature of the soot.

148. Sulphur dioxide can readily be obtained in the liquid state by passing the gas through a U-tube immersed in a freezing mixture of ice and salt, since, by mere cooling to -10° under the ordinary atmospheric pressure, it is converted into a colorless limpid liquid. On being exposed to the air at ordinary temperatures, this liquid evaporates with great rapidity, and consequently occasions very intense cold.

If a quantity of the liquid be poured into water, the temperature of which is a few degrees above 0° , a portion will evaporate at once, another portion will dissolve in the water, and a third portion of the heavy, oily liquid will sink to the bottom of the vessel. If the portion which has thus subsided be stirred with a glass rod, it will boil at once, and the temperature of the water will be so much reduced that a portion, or even the whole, of the water will be frozen.

The volumetric composition of sulphur dioxide is one volume of sulphur vapor and two volumes of oxygen condensed to two volumes of the compound gas. The gas is very readily soluble in water, and may be regarded as combining with a portion of the water to form sulphurous acid, the formula of which would be H_2SO_3 . While no acid of this composition is known in a free condition, the solution of the gas in water has all the properties of an acid, and a large number of salts derived from this acid are known, many of which are made by treating the aqueous solution of the gas with bases. Sulphur dioxide thus appears to be the anhydride of this sulphurous acid, —



and it is often termed *sulphurous anhydride*, in accordance with this view. In ordinary language, however, the term *sulphurous acid* is used to denote the gas SO_2 .¹

149. Sulphur dioxide is a powerful *disinfecting*, *antiseptic*, and *germicide* agent. It retards processes of putrefaction and fermentation, and is largely used for fumigation in cases of contagious diseases; of much importance, also, is its power of *bleaching* vegetable colors. It is extensively employed in bleaching articles of straw, wool, silk, etc., which would be injured by chlorine. The bleaching may be effected by immersion in the aqueous solution of sulphurous acid or by exposure to the fumes of burning sulphur. In the latter case the articles to be bleached must be moistened. The dry oxide does not bleach. In most cases, sulphurous acid does not destroy the coloring matters as chlorine does, but seems to combine with them to form colorless compounds. These colorless compounds can be broken up, with restoration of color, by exposing them to the action of various chemical agents capable of setting free sulphurous acid.

Exp. 78. — Bleach a red rose by hanging it in a bottle in which sulphur has been burned, or by holding it over burning sulphur. Immerse the bleached rose in dilute sulphuric acid, dry and warm it, and observe that the color will reappear.

In the arts, the process of bleaching is usually conducted in large chambers, in which the slightly moistened articles are hung while sulphur is burned below. The damp goods absorb the gas, and gradually become white. A practical illustration of the restoration of color by chemical agents is seen in the reproduction of the original yellow color of the wool when new flannel is washed. The alkali of the soap removes the sulphurous acid, and the color reappears.

150. Sulphur trioxide, or sulphuric oxide (SO_3), may be prepared by the direct oxidation of sulphur dioxide. If a mixture of sulphurous anhydride and oxygen be passed over heated, very finely divided platinum (platinum sponge), the two gases

¹ The substances now designated as *acid anhydrides* were formerly called *acids*, as has been intimated in § 71. In the case of sulphurous, arsenious, and carbonic anhydrides, the popular names have such currency that they will frequently be employed in this manual in cases where no ambiguity or doubt can arise as to the meaning of the terms.

unite to form sulphur trioxide, which condenses in the cooled receiver. It is a white, waxlike solid, crystallizing in silky fibers, resembling asbestos. If a bit of it be thrown into water, the water hisses as if a hot iron had been thrust into it; and the sulphur trioxide unites with a portion of the water, with the evolution of great heat, to form sulphuric acid. It thus appears as the anhydride of sulphuric acid, and is often called *sulphuric anhydride*. The solid anhydride has so great an attraction for water, that it can be preserved only in dry tubes sealed at the lamp.

151. **Sulphuric acid (H_2SO_4)** is one of the most important products of chemical manufacture, and is made in enormous quantities. In the same way that the metal iron may be said to be the basis of all mechanical industries, sulphuric acid lies at the foundation of the chemical arts. By means of sulphuric acid, the chemist, either directly or indirectly, prepares almost everything with which he has commonly to deal.

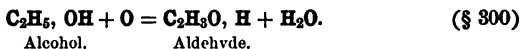
152. Sulphuric acid is made by oxidizing sulphur dioxide in the presence of moisture. This oxidation cannot be effected *directly* in the air in any economical manner: it is necessary to use some *oxidizing agent*.

This term *oxidizing agent* is applied to a substance which habitually and readily imparts oxygen to other bodies with which it is brought into contact: on the other hand, a substance which habitually and readily takes oxygen out of other substances with which it is brought into contact is called a *reducing agent*. Nitric acid, such as was prepared in Exp. 33, § 64, is a very powerful oxidizing agent; and sulphuric acid might be made by boiling sulphur for a long time in nitric acid. This method would, however, not be practicable on a large scale. Nitric acid also oxidizes sulphur dioxide.

153. **Oxidation and Reduction.**—The terms *oxidation* and *reduction* are often used in a much wider sense than is implied by the above statement. As an example of another use of the terms, we may take the case of the two chlorides of tin. If by some chemical process the stannous oxide (SnO) were converted into the stannic oxide (SnO_2), we should legitimately speak of this as a process of oxidation; if, now, the stannous chloride ($SnCl_2$), in which the atom of tin, as in stannous oxide, is bivalent, be converted into the stannic chloride ($SnCl_4$), in which the atom of tin, as in stannic oxide, is quadrivalent, we speak of this process also as one of oxidation, although there is no oxygen

in either compound. If the reverse action were performed, and the stannic chloride were converted into the stannous chloride, we would speak of the process as one of reduction. When ferrous compounds, in which the atoms of iron are bivalent, are converted into ferric compounds, in which they are trivalent, and when the salts of chromium, in which the atom of chromium has a valence of 3, are changed to chromates, in which the valence of chromium is 6, by means of *oxidizing agents*, and, in general, *where an element can occur with two different degrees of valence, the passing from the lower to the higher is said to be brought about by an oxidizing action, and the passing from the higher to the lower by a reducing action.* No objection can be made to the use of the terms *reduction* and *reducing agent* in this way, although the terms *oxidation* and *oxidizing agent* may in some cases be manifestly improper. Such use of the terms originated when the dualistic idea that the salts contained the corresponding oxides was generally accepted; and from such salts as sulphates, etc., the use was extended even to chlorides.

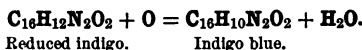
Other characteristic examples of oxidizing and reducing actions are as follows:—



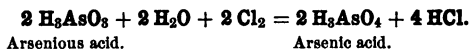
Here the aldehyde contains no more oxygen than the alcohol, but it contains less hydrogen; a portion of the hydrogen having been oxidized, and removed as water.



Here the hydrogen acts as a reducing agent, not by appropriating oxygen, but by actually entering into the molecule. When the reduced or white indigo is exposed to the air, it becomes blue. The white indigo is said to be oxidized, although the action is really a removal of hydrogen, as seen in the following equation:—

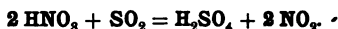


Chlorine is often spoken of as an oxidizing agent. It acts in two distinct ways, which may be illustrated as follows:—



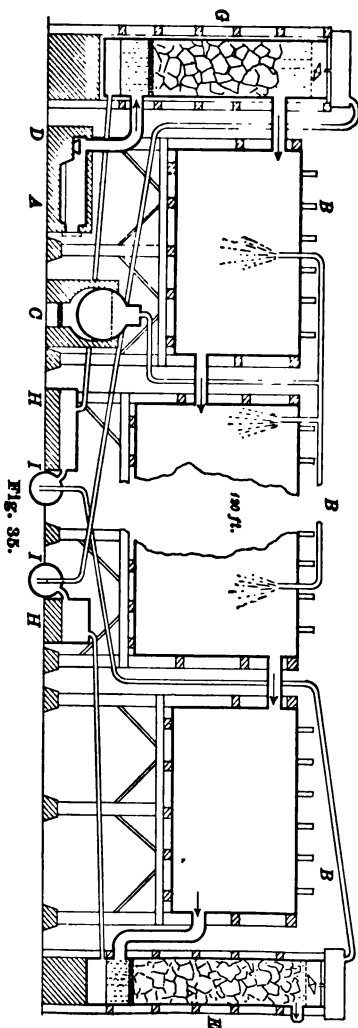
In the first equation, chlorine enters* into the compound oxidized: the mercurous chloride is said to be *oxidized* to mercuric chloride. In the second equation, the chlorine acts by appropriating the hydrogen of two molecules of water, leaving the oxygen free to enter into combination.

Exp. 79. — Charge a bottle, of the capacity of a liter or more, with sulphurous gas by burning in it a bit of sulphur. Fasten a shaving, or, better, a tuft of gun cotton, upon a glass rod or tube bent at one end in the form of a hook; wet the shaving in concentrated nitric acid, and hang it in the bottle of sulphurous gas. Red fumes of nitrogen tetroxide will immediately form about the nitric acid, and will gradually fill the bottle. The appearance of the red-brown fumes shows that there has been a loss of oxygen on the part of the nitric acid. The reaction may be thus written:—



In a short time the reddish brown color may disappear, and a crystalline substance form on the sides of the bottle. When this formation is noticed, if a little water be shaken in the bottle, the white crystals will dissolve with effervescence, and the red-brown fumes will again appear. On testing the water with blue litmus, it will be found to have a strongly acid reaction, due to the presence of sulphuric acid. In this case, sulphur dioxide is an example of a reducing agent. In the presence of much moisture, it can take oxygen from all the higher oxides (and acids) of nitrogen, as HNO_3 , NO_2 , N_2O_5 , and HNO_2 , and reduce them all to nitric oxide (NO).

154. The manufacture of sulphuric acid, shown in a general way in Fig. 35, depends on the fact illustrated in Exp. 79, § 153. Sulphur dioxide, obtained by burning sulphur, or, more commonly, a compound of sulphur and iron known as *iron pyrites*, in a suitable furnace, A, is conducted, together with a



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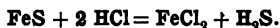
Fig. 32.

Hydrogen sulphide is soluble in water to a considerable extent, and is consequently taken up by the water in the absorption bottle. The solution thus obtained, known as *sulphuretted hydrogen water*, is much employed as a reagent in chemical laboratories.

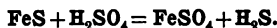
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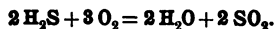
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Exp. 71. — To the delivery tube of the gas bottle employed in generating hydrogen sulphide, attach a drying tube containing fragments of calcium chloride, and with the tube connect a piece of No. 6 glass tubing drawn out to a fine point. When the apparatus is full of the gas, apply a match to the end of the tube. The gas will take fire, and burn with a blue flame. If a dry bottle be held over the flame, the walls will become coated with moisture, which will have an acid reaction and will redden blue litmus paper.

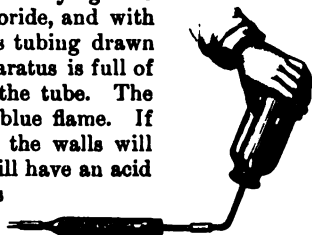
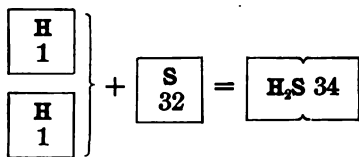


Fig. 33.

The jet of hydrogen sulphide should not be lighted until all the air is expelled from the apparatus, as this gas forms an explosive mixture with air.

138. Hydrogen sulphide is readily decomposed by heat, as may be shown by passing a current of the gas through a glass tube, heated for a portion of its length. The gas will be separated into hydrogen and sulphur: the latter will be deposited on the cold portion of the tube.

Analysis has proved that the composition of hydrogen sulphide, both by volume and by weight, may be expressed by the following diagram, in which the symbol S represents a unit volume of sulphur in the state of vapor: —

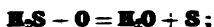


The product is similar, in respect to volumetric composition, to water vapor or dry steam.

139. Hydrogen sulphide is very poisonous. When respired in the pure state, it quickly proves fatal; and it is very deleterious, even though largely diluted with atmospheric air. Nausea and headache are often produced when an atmosphere even slightly contaminated with it is breathed for any length of time. It is therefore best, when experimenting with it, to operate where there is a free circulation of air.

The gas exists as a natural constituent of some mineral waters which are thence called sulphurous, such as the Virginia Sulphur Springs, and the mineral springs at Sharon, N.Y. It is also found in the air and water of foul sewers, and where animal matter is undergoing putrefaction.

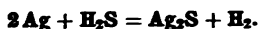
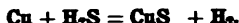
140. Water dissolves about three times its own volume of hydrogen sulphide at ordinary temperatures. This solution (Exp. 70, § 136) is transparent and colorless when freshly prepared, but when kept, it gradually becomes turbid through deposition of sulphur. Oxygen from the air unites with the hydrogen and sets free sulphur.



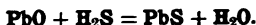
so that after a time the solution may no longer contain any of the gas. The moist gas and its aqueous solution have a slight acid reaction upon litmus.

141. When moist hydrogen sulphide comes in contact with certain of the metals, it is decomposed.

Exp. 72. — Place a drop of sulphuretted hydrogen water (Exp. 70, § 136) upon a bright piece of copper, lead, or silver. The metal will quickly become black. The sulphur of the hydrogen sulphide unites with the metal to form a sulphide of the metal, while the hydrogen escapes, or we may say that the metal *replaces* the hydrogen in the hydrogen sulphide.



Exp. 73. — Place in a test tube a little litharge (lead monoxide); pour upon it a teaspoonful of hydrogen sulphide solution. The brown litharge at once becomes black. Lead sulphide is formed, and water is set free, —

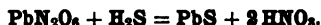


Similar reactions take place on treating many other metallic oxides with hydrogen sulphide.

From a solution of any compound of these metals, hydrogen sulphide will throw down the sulphide of the metal.

Exp. 74. — Dissolve a small crystal of lead nitrate in a test tube half full of water, and to this solution add a few drops of the sulphu-

retted hydrogen water. Lead sulphide is thrown down as a black precipitate, and nitric acid is set free :—



142. Since the sulphides of many elements are, like those of lead, copper, and silver, insoluble in water and dilute acids, hydrogen sulphide will precipitate them from solutions of their salts. Many of these precipitates are black, like that of lead; but sulphide of antimony is orange, sulphide of cadmium yellow, and zinc sulphide is white. The precipitates thus obtained often serve for the detection and characterization of the corresponding elements.

Exp. 75.— Take 20 cc. of a solution of each of the following substances: copper sulphate (CuSO_4), antimony chloride (SbCl_3), cadmium chloride (CdCl_2), and zinc sulphate (ZnSO_4); place the solutions in separate test tubes, and pass hydrogen sulphide through each of the solutions in turn.

A common method of detecting the presence of hydrogen sulphide depends upon the decomposition of lead acetate, lead sulphide being formed.

Exp. 76.— Moisten a piece of filter paper with a solution of lead acetate, and expose it to hydrogen sulphide from any source. The paper will immediately be blackened through the formation of lead sulphide, which often exhibits a peculiar lustrous appearance.

On account of its power of precipitating various metallic sulphides, hydrogen sulphide is much used in the analytical laboratory as a reagent.

143. Hydrogen sulphide is comparatively unstable, and may readily be decomposed in a variety of ways. When simply heated, it is decomposed into its elements, as has been seen already. All substances which readily give up oxygen decompose it, the oxygen uniting with the hydrogen to form water, while sulphur is set free. Chlorine, bromine, and iodine vapor instantly decompose it, uniting with its hydrogen to form the halogen acids, and setting sulphur free. It is thus seen to be a much less stable compound than the corresponding hydrogen oxide, water.

144. The chemical action of hydrogen sulphide shows that it belongs to the class of bodies called acids (§ 67). Its action on oxides (as in Exp. 73, § 141) is similar to the action of acids upon basic oxides, a sulphide and water being formed. The sulphides may thus be regarded as derived from hydrogen sulphide by the replacement of its hydrogen atoms. There is a class of bodies which can be regarded as derived

from hydrogen sulphide by the replacement of but one of its atoms of hydrogen by metallic atoms. They are known as the *hydrosulphides* or *sulphydrates*. For example, **KSH** (potassium hydrosulphide) and **NaSH** (sodium hydrosulphide) may be regarded as bearing the same relation to hydrogen sulphide that their hydroxides bear to water. On account of the fact that hydrogen sulphide forms salts in the same general way as acids, it is sometimes called *sulphydic acid*.

A compound of sulphur and hydrogen (hydrogen disulphide) analogous to hydrogen dioxide is known. Its composition may be represented by the formula H_2S_2 .

145. Sulphur and Oxygen.—Of the compounds of sulphur and oxygen, the most important are *sulphur dioxide* or *sulphurous oxide*, and *sulphur trioxide* or *sulphuric oxide*.

146. Sulphur dioxide (SO_2), commonly called *sulphurous acid*, is produced whenever sulphur is burned in air or in oxygen gas.

Exp. 77.—Light a piece of sulphur in a deflagrating spoon, and suspend the latter in a half-liter bottle full of air. On examining the contents of the bottle, after the sulphur has ceased to burn, there will be found an irritating, suffocating gas having the peculiar odor which is familiar as that of a burning match. The bottle is now full of sulphurous oxide mixed with the nitrogen originally present in the air.



Fig. 34.

An easier method of preparing pure sulphur dioxide is by depriving common sulphuric acid of part of its oxygen. This result can be effected by a variety of reducing or deoxidizing agents. For example, when concentrated sulphuric acid is heated with metallic copper, there is formed a sulphate of the metal, water, and sulphurous acid:—



Certain other metals, such as mercury, for example, can be employed instead of copper, the reaction being similar.

147. Sulphur dioxide is a transparent and colorless gas. It is irrespirable and suffocating, and when mixed with air, even in small proportion, occasions violent coughing. It is not inflammable, but, on the contrary, it stops combustion; nor does it readily give up its oxygen

The flame of a candle is immediately extinguished on being immersed in the gas, just as it is by nitrogen. A useful application of this property of sulphur dioxide is in extinguishing burning chimneys. A handful of fragments of sulphur being thrown into the fire, and the openings of the fireplace closed in such manner that little or no air shall enter the chimney, excepting that which passes through the fire, the chimney will quickly become filled with an atmosphere of sulphurous gas mixed with nitrogen from the air employed in burning the sulphur, and the burning soot upon the walls of the chimney will be extinguished.

It is, of course, essential that the chimney should then be closed at the top, so that air may be excluded, and the chimney kept full of the fire-extinguishing atmosphere until its walls shall have cooled to below the kindling temperature of the soot.

148. Sulphur dioxide can readily be obtained in the liquid state by passing the gas through a U-tube immersed in a freezing mixture of ice and salt, since, by mere cooling to -10° under the ordinary atmospheric pressure, it is converted into a colorless limpid liquid. On being exposed to the air at ordinary temperatures, this liquid evaporates with great rapidity, and consequently occasions very intense cold.

If a quantity of the liquid be poured into water, the temperature of which is a few degrees above 0° , a portion will evaporate at once, another portion will dissolve in the water, and a third portion of the heavy, oily liquid will sink to the bottom of the vessel. If the portion which has thus subsided be stirred with a glass rod, it will boil at once, and the temperature of the water will be so much reduced that a portion, or even the whole, of the water will be frozen.

The volumetric composition of sulphur dioxide is one volume of sulphur vapor and two volumes of oxygen condensed to two volumes of the compound gas. The gas is very readily soluble in water, and may be regarded as combining with a portion of the water to form sulphurous acid, the formula of which would be H_2SO_3 . While no acid of this composition is known in a free condition, the solution of the gas in water has all the properties of an acid, and a large number of salts derived from this acid are known, many of which are made by treating the aqueous solution of the gas with bases. Sulphur dioxide thus appears to be the anhydride of this sulphurous acid, —



and it is often termed *sulphurous anhydride*, in accordance with this view. In ordinary language, however, the term *sulphurous acid* is used to denote the gas SO_2 .¹

149. Sulphur dioxide is a powerful *disinfecting*, *antiseptic*, and *germicide* agent. It retards processes of putrefaction and fermentation, and is largely used for fumigation in cases of contagious diseases; of much importance, also, is its power of *bleaching* vegetable colors. It is extensively employed in bleaching articles of straw, wool, silk, etc., which would be injured by chlorine. The bleaching may be effected by immersion in the aqueous solution of sulphurous acid or by exposure to the fumes of burning sulphur. In the latter case the articles to be bleached must be moistened. The dry oxide does not bleach. In most cases, sulphurous acid does not destroy the coloring matters as chlorine does, but seems to combine with them to form colorless compounds. These colorless compounds can be broken up, with restoration of color, by exposing them to the action of various chemical agents capable of setting free sulphurous acid.

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In the arts, the process of bleaching is usually conducted in large chambers, in which the slightly moistened articles are hung while sulphur is burned below. The damp goods absorb the gas, and gradually become white. A practical illustration of the restoration of color by chemical agents is seen in the reproduction of the original yellow color of the wool when new flannel is washed. The alkali of the soap removes the sulphurous acid, and the color reappears.

150. Sulphur trioxide, or sulphuric oxide (SO_3), may be prepared by the direct oxidation of sulphur dioxide. If a mixture of sulphurous anhydride and oxygen be passed over heated, very finely divided platinum (platinum sponge), the two gases

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152. Sulphuric acid is made by oxidizing sulphur dioxide in the presence of moisture. This oxidation cannot be effected *directly* in the air in any economical manner: it is necessary to use some *oxidizing agent*.

This term *oxidizing agent* is applied to a substance which habitually and readily imparts oxygen to other bodies with which it is brought into contact: on the other hand, a substance which habitually and readily takes oxygen out of other substances with which it is brought into contact is called a *reducing agent*. Nitric acid, such as was prepared in Exp. 33, § 64, is a very powerful oxidizing agent; and sulphuric acid might be made by boiling sulphur for a long time in nitric acid. This method would, however, not be practicable on a large scale. Nitric acid also oxidizes sulphur dioxide.

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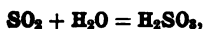
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in either compound. If the reverse action were performed, and the stannic chloride were converted into the stannous chloride, we would speak of the process as one of reduction. When ferrous compounds, in which the atoms of iron are bivalent, are converted into ferric compounds, in which they are trivalent, and when the salts of chromium, in which the atom of chromium has a valence of 3, are changed to chromates, in which the valence of chromium is 6, by means of *oxidizing agents*, and, in general, *where an element can occur with two different degrees of valence, the passing from the lower to the higher is said to be brought about by an oxidizing action, and the passing from the higher to the lower by a reducing action.* No objection can be made to the use of the terms *reduction* and *reducing agent* in this way, although the terms *oxidation* and *oxidizing agent* may in some cases be manifestly improper. Such use of the terms originated when the dualistic idea that the salts contained the corresponding oxides was generally accepted; and from such salts as sulphates, etc., the use was extended even to chlorides.

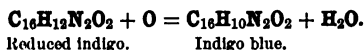
(Other characteristic examples of oxidizing and reducing actions are as follows:—



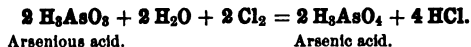
Here the aldehyde contains no more oxygen than the alcohol, but it contains less hydrogen; a portion of the hydrogen having been oxidized, and removed as water.



Here the hydrogen acts as a reducing agent, not by appropriating oxygen, but by actually entering into the molecule. When the reduced or white indigo is exposed to the air, it becomes blue. The white indigo is said to be oxidized, although the action is really a removal of hydrogen, as seen in the following equation:—

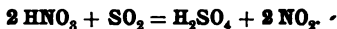


Chlorine is often spoken of as an oxidizing agent. It acts in two distinct ways, which may be illustrated as follows:—



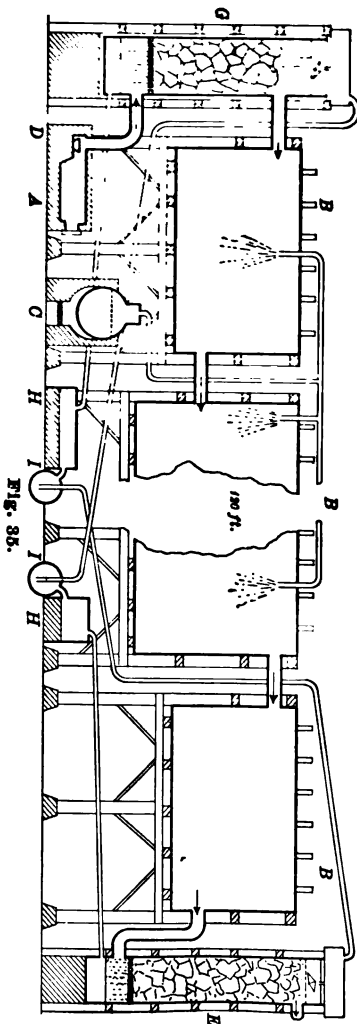
In the first equation, chlorine enters into the compound oxidized: the mercurous chloride is said to be *oxidized* to mercuric chloride. In the second equation, the chlorine acts by appropriating the hydrogen of two molecules of water, leaving the oxygen free to enter into combination.

Exp. 79. — Charge a bottle, of the capacity of a liter or more, with sulphurous gas by burning in it a bit of sulphur. Fasten a shaving, or, better, a tuft of gun cotton, upon a glass rod or tube bent at one end in the form of a hook; wet the shaving in concentrated nitric acid, and hang it in the bottle of sulphurous gas. Red fumes of nitrogen tetroxide will immediately form about the nitric acid, and will gradually fill the bottle. The appearance of the red-brown fumes shows that there has been a loss of oxygen on the part of the nitric acid. The reaction may be thus written:—



In a short time the reddish brown color may disappear, and a crystalline substance form on the sides of the bottle. When this formation is noticed, if a little water be shaken in the bottle, the white crystals will dissolve with effervescence, and the red-brown fumes will again appear. On testing the water with blue litmus, it will be found to have a strongly acid reaction, due to the presence of sulphuric acid. In this case, sulphur dioxide is an example of a reducing agent. In the presence of much moisture, it can take oxygen from all the higher oxides (and acids) of nitrogen, as HNO_3 , NO_2 , N_2O_5 , and HNO_3 , and reduce them all to nitric oxide (NO).

154. The manufacture of sulphuric acid, shown in a general way in Fig. 35, depends on the fact illustrated in Exp. 79, § 153. Sulphur dioxide, obtained by burning sulphur, or, more commonly, a compound of sulphur and iron known as *iron pyrites*, in a suitable furnace, *A*, is conducted, together with a

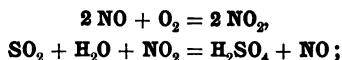


large excess of air, into a series of enormous chambers, *B*, into which jets of steam can be blown from the boiler, *C*. The chambers are made of sheet lead, a metal on which cold sulphuric acid has little action. Nitrous fumes are supplied either by allowing nitric acid to fall in fine streams through the incoming current of sulphurous acid and air, or from the decomposition of sodium nitrate, in an iron pot, *D*, in the sulphur furnace.

The reactions taking place in the lead chambers are very complicated, being influenced by the quantities of the reacting substances, and by the temperature. The nitrous fumes, in the presence of moisture, oxidize the sulphur dioxide to sulphuric acid, which falls to the bottom of the chamber, while they are themselves reduced to nitrogen dioxide, which is set free.



The oxygen of the air which is in the chambers, and which enters with the other gases, converts the nitrogen dioxide (NO) again into nitrogen tetroxide (NO_2), which reacts in turn upon a new portion of sulphur dioxide to form sulphuric acid,—



and the process thus goes on through the whole series of leaden chambers, the very small portion of nitric acid introduced at first being sufficient to prepare a large quantity of sulphuric acid. In reality, the oxygen employed in converting the sulphur dioxide into sulphuric acid all comes from the air, excepting a very little at first: the nitrous fumes serve only as a conveyer of oxygen. The NO takes oxygen from the air and transfers it to the sulphur dioxide, which is, by itself and unaided, incapable of combining with oxygen. It will, of course, be understood, that although we trace out these reactions as if they were consecutive, they are really, so far as we know, simultaneous.

Theoretically, a single portion of nitric acid would be sufficient to effect the conversion of an unlimited amount of sulphur dioxide into sulphuric acid, but practically this power is qualified by a variety of circumstances. It is found to be impossible, for example, to introduce new portions of air into the mixture of sulphur dioxide and nitric oxide for an indefinite period; for at a certain point these gases become so loaded down with nitrogen derived from the air already consumed, that they are as good as lost in it. In general, the flow of gases is so regulated, that all the sulphur dioxide shall be oxidized, and that nothing but nitrogen dioxide and the waste nitrogen shall pass out of the last leaden chamber. This nitrogen dioxide may be absorbed in strong sulphuric acid, and saved, by causing the gases from the leaden chambers to pass through a tower, *E* (known

as a *Gay Lussac tower*), filled with pieces of coke, over which the acid is made to trickle; and the solution of nitrogen dioxide may be put to use by causing the hot mixture of sulphurous gas and air from the furnace to pass through another tower, *G* (known as *Glover's tower*), which is placed between the furnace and the first leaden chamber, and packed with flints or pieces of fire brick, over which the acid charged with the nitrous fumes is made to trickle, while at the same time it is somewhat diluted with water. The letters *H*, in the figure, denote boxes into which the liquids dripping from the towers flow. From time to time, these liquors are run into strong cylinders, *I*, whence they are forced to the tops of the towers by means of compressed air.

155. The foregoing method of making sulphuric acid may be illustrated as follows: A large glass flask or globular receiver of several liters' capacity (*A*, Fig. 36) is closed with a cork or glass plate pierced with five holes, through each of which passes a glass tube. Four of these tubes reach nearly to the bottom of the receiver; one

(*e*) should pass but a short distance below the cork, as it serves merely as an exit tube for any excess of gas. One of the tubes is connected with a flask (*a*) containing copper turnings and strong sulphuric acid for the generation of sulphur dioxide (§ 146); another, with a flask (*b*) containing copper turnings, and provided with a thistle tube, through which nitric acid can be poured for the generation of nitrogen dioxide (Exp. 27, § 53); and the third, with a flask

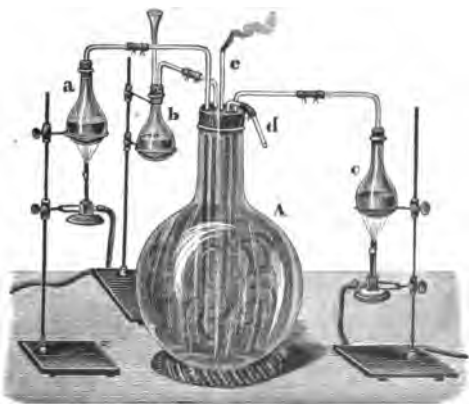


Fig. 36.

(*c*) containing water for the evolution of steam. The fourth tube (*e*) allows the unused nitrogen to escape, and, by forcing air from time to time through *d*, the process may be made continuous. Everything being in readiness, nitrogen dioxide is generated in *b*; and, as the gas passes into the receiver, it unites with the oxygen, and the red-brown fumes of nitrogen tetroxide are seen. Sulphur dioxide is now generated in flask *a*, and made to pass into the receiver. So long as there is no moisture present, no action takes place: but, when steam is made

to pass in by boiling the water in the flask *c*, a reaction occurs, a white cloud appears in the receiver, and the brown color of the vapor disappears to a great extent; the sulphur dioxide reducing the nitrogen tetroxide to nitrogen dioxide, with the formation of sulphuric acid. If but little steam be employed, a solid compound having the composition SO_3HNO_2 (nitrosyl sulphuric acid) is produced, which reacts with water to form sulphuric acid and set nitrogen oxides free.

156. The acid obtained in the lead chambers as described above is still dilute. It is concentrated by evaporating it, first in leaden pans, until a degree of concentration is reached at which the lead would be corroded by the hot acid, and finally in large glass retorts or in platinum stills, until it has nearly the composition H_2SO_4 .

The acid thus boiled down is the concentrated sulphuric acid, or oil of vitriol, of commerce. Its specific gravity is usually about 1.83. It contains in solution a certain quantity of lead sulphate and a variety of other impurities. For most purposes, however, it will answer as well as the pure acid. It is a heavy, oily, colorless, and odorless liquid, boiling at about 330° . Concentrated sulphuric acid is not volatile as such, though it may readily be boiled away at a high temperature. It undergoes *dissociation* at from 325° to 330° , and is resolved into the anhydride and water; thus, —



But these compounds immediately reunite on cooling. That this volatilization is not true boiling, is shown by the fact that even under reduced pressure it takes place only at the same temperature as when under the atmospheric pressure. A similar decomposition appears to occur in respect to carbonic and sulphurous acids, though at much lower temperatures.

157. At the ordinary temperature, sulphuric acid does not vaporize, but, on the contrary, greedily absorbs water from the air: hence it is used for drying gases and in the desiccators employed by chemists. In moist weather its bulk may increase, by this absorption of moisture from the air, to the extent of a quarter or more in the course of a single day, and, by longer exposure, a still larger quantity of water will be taken up.

The acid must always be kept, therefore, in tightly stoppered bottles.

158. Sulphuric acid unites with liquid water with great energy, much heat being evolved at the moment of combination. During the union a certain amount of condensation occurs; the mixture, when cold, occupying less space than was previously occupied by the acid and the water. The water and acid may be mixed in all proportions, being mutually soluble one in the other.

In mixing water and sulphuric acid, the acid should always be poured into the water in a fine stream, not the water into the acid,—the water being meanwhile stirred. In this way the heavy acid has an opportunity to mix with the water as it sinks down through it. If, by any accident, water were to fall upon sulphuric acid, it would float on top of it, and great heat would be developed at the point of contact of the two liquids. If the quantities of acid and water were large, sudden bursts of steam would be occasioned, and serious damage might arise from the scattering about of portions of the acid.

Exp. 80.—Place in a beaker of about 250 cc. capacity 30 cc. of water. In accordance with the directions above given, pour into the water 120 g. of concentrated sulphuric acid, and stir the mixture with a narrow test tube containing a teaspoonful of water. So much heat will be evolved during the union of the water and the acid, that the water in the test tube will boil.

When sulphuric acid reacts with water, chemical combination takes place, and distinct chemical compounds are formed which can be obtained under certain conditions in the crystalline state. The composition of these hydrates may be represented by the formulas H_2SO_4 and H_4SO_4 . They are sometimes called *normal sulphuric acid* and *tetrahydroxyl sulphuric acid*. In mixing sulphuric acid with water, the greatest amount of heat and the maximum contraction in volume are observed when such proportions are used as would form H_2SO_4 . (See note, p. 394a.)

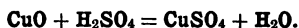


159. Sulphuric acid is one of the most powerful acids known. When diluted with a thousand times its bulk of water, it is still capable of reddening blue litmus. It sets free most of the other acids from their salts, in the same way that we have

seen it set free nitric acid from sodium nitrate in Exp. 33, § 64. It is intensely caustic and corrosive, and quickly chars and destroys most vegetable and animal substances.

Exp. 81.—Into a test tube pour a tablespoonful of sulphuric acid and immerse in it a splinter of wood. The wood will blacken as if charred by fire, and the acid will become dark-colored. Wood is composed of carbon, hydrogen, and oxygen; and since sulphuric acid unites with compounds of hydrogen and oxygen, rather than with carbon, a portion of the latter is left free. Some carbonaceous matter is, however, dissolved by the acid, and darkens it. The acid of commerce is often dark-colored from fragments of straw or other organic matter having accidentally fallen into it.

160. Sulphates.—Strong sulphuric acid is reduced to sulphurous acid when heated with charcoal or the ordinary metals, as was seen in the preparation of sulphur dioxide, the metals themselves being converted into oxides, which, in turn, react with more of the acid to form sulphates and set free water:—



The action of the dilute acid upon many metals, metallic oxides, and hydroxides, is similar to that of hydrochloric acid; the hydrogen atoms of the acid being replaced, and sulphates formed. Many of these salts of sulphuric acid are of great economic importance.

In the formation of the sulphates of those metals which replace hydrogen atom for atom (§ 86), it is not necessary that both atoms of hydrogen in the sulphuric acid (H_2SO_4) should be replaced. As has been seen already (§ 61), we may have a compound in which sodium replaces only one of the hydrogen atoms, namely, NaHSO_4 (sodium acid sulphate); for sulphuric acid is a dibasic acid (§ 70).

161. Fuming Sulphuric Acid.—On adding sulphur trioxide to ordinary sulphuric acid, there would be formed a fuming solution which some chemists have regarded as disulphuric or pyrosulphuric acid,—



For commercial purposes, the fuming liquid is prepared, either by dissolving the anhydride in strong sulphuric acid, or by distilling *ferric sulphate* in earthen retorts. Formerly it was made by distilling ferrous sulphate, the old name of which was *green vitriol*: hence the

origin of the name *oil of vitriol*, which, in England and this country, has come to be applied solely to the common acid H_2SO_4 . At one time this fuming (or *Nordhausen*) acid was a product of no little importance, but the chief use to which it is now put is for dissolving indigo. On heating fuming sulphuric acid, sulphur trioxide is given off from it, and may be collected in an ice-cold receiver, while ordinary sulphuric acid remains.

162. There are a large number of hydrogen, oxygen, and sulphur compounds having acidic properties. Most of them have but little practical importance, and a description of them would be out of place in an elementary manual. Thiosulphuric acid ($\text{H}_2\text{S}_2\text{O}_3$) deserves special mention, because it is often met with in the form of the sodium salt ($\text{Na}_2\text{S}_2\text{O}_3$), commonly called *hyposulphite of soda*, which is used by bleachers as an *antichlor* to remove any excess of chlorine which might cling to the bleached goods and tend to weaken them by corrosion. It is used also to "fix the picture" in certain processes of photography, since it readily dissolves the silver compounds on which light has not acted, and leaves the image intact. Sodium thiosulphate is often made by oxidizing calcium sulphide, as found in the *soda waste* which accumulates at alkali works; and it may readily be prepared by boiling sulphur with *soda lye*, and passing sulphur dioxide into the mixture of hydroxide and sulphide.



Thiosulphuric acid itself has never been isolated, though many of its salts are known. Closely allied to this acid is a remarkable series of acid compounds, known as the *polythionic acids*; viz., dithionic acid ($\text{H}_2\text{S}_2\text{O}_6$), trithionic acid ($\text{H}_2\text{S}_3\text{O}_6$), tetrathionic acid ($\text{H}_2\text{S}_4\text{O}_6$), and pentathionic acid ($\text{H}_2\text{S}_5\text{O}_6$). Taken in connection with the other oxyacids of sulphur, — viz., hyposulphurous acid (H_2SO_2), sulphurous acid (H_2SO_3), sulphuric acid (H_2SO_4), and thiosulphuric acid ($\text{H}_2\text{S}_2\text{O}_3$), — the polythionic acids afford a very striking example of the law of multiple proportions, already studied in the case of the five oxides of nitrogen (§ 62).

163. **Sulphur and Chlorine.** — Of the numerous compounds of sulphur and the halogen elements, only sulphurous chloride (S_2Cl_2) is of practical importance. It is formed when chlorine is passed over melted sulphur, and is a reddish liquid, fuming strongly in the air; and, like all the halide compounds of sulphur, it is easily decomposed by water.



Sulphurous chloride was used at one time in the vulcanization of caoutchouc by what was known as the *cold process*.

**SELENIUM (Se), ATOMIC WEIGHT, 78.4; AND TELLURIUM (Te),
ATOMIC WEIGHT, 124.**

164. These elements are rare, and at present of little industrial importance; but to the chemist they are exceedingly interesting, on account of the close resemblance they bear to sulphur.

165. **Selenium** is never found in any considerable quantity in any one place. Traces of it occur in many varieties of native sulphur and in various metallic sulphides. In its properties and in its chemical behavior, selenium resembles sulphur in many respects, while in others it is like tellurium. Like sulphur and oxygen, it occurs in distinct allotropic modifications (§§ 119, 133): it forms with hydrogen a compound, hydrogen selenide (H_2Se), resembling hydrogen sulphide; it forms an acid, selenic acid (H_2SeO_4), resembling sulphuric acid. There are *selenates* possessing characters similar to the sulphates, and crystallizing in the same form; and, according to a principle illustrated by the halogen group, selenium, which has the higher atomic weight (78.4), is a weaker chemical agent than sulphur (32).

166. **Tellurium** occurs in nature even more rarely than selenium. Sometimes it is found in the free state, but more generally in combination with the heavy metals, such as gold, silver, lead, copper, and bismuth. Tellurium is of a silver-white color and glittering, metallic luster. In many of its physical characters it would seem to be allied to certain metals, but its chemical properties place it in the same group with sulphur and selenium. It forms compounds with hydrogen, oxygen, and with other elements which resemble the corresponding sulphur compounds.

167. The elements sulphur, selenium, and tellurium, in their chemical properties, are closely allied to oxygen. The formulas of a few of the compounds of these elements are here given to bring out some of their points of resemblance:—

| H_2O | H_2S | H_2Se | H_2Te |
|------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|
| Water. | Hydrogen sulphide. | Hydrogen selenide. | Hydrogen telluride. |
| FeO | FeS | FeSe | FeTe |
| Iron oxide. | Iron sulphide. | Iron selenide. | Iron telluride. |
| $(\text{C}_2\text{H}_5)_2\text{O}$ | $(\text{C}_2\text{H}_5)_2\text{S}$ | $(\text{C}_2\text{H}_5)_2\text{Se}$ | $(\text{C}_2\text{H}_5)_2\text{Te}$ |
| Ether (Ethyl oxide). | Ethyl sulphide. | Ethyl selenide. | Ethyl telluride. |

The four elements, oxygen, sulphur, selenium, and tellurium, form a natural group of chemically similar bodies, analogous to that formed by the halogens (§ 117). As with the elements of the halogen group, so here a gradation of the physical and chemical properties is apparent, which coincides with the gradation of the atomic weights of the members of the oxygen group.

CHAPTER XI.

COMBINATION BY VOLUME, MOLECULAR WEIGHT, ATOMIC WEIGHT, SPECIFIC HEAT.

168. A comparison of the formulas representing the volumetric composition of all the well-defined compound gases and vapors which have thus far been studied, will bring into clear view some of the general facts relating to **combination by volume**.

It has been established by experiment that the following compounds are formed by the chemical union, without condensation, of equal volumes of the two elements which enter into each compound:—

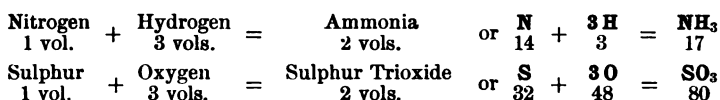
| | | | | | | | | | | |
|--------------------|---|--------------------|---|------------------------------|----|------------------|---|---------------------|---|----------------------|
| Hydrogen 1 vol. | + | Chlorine 1 vol. | = | Hydrochloric Acid 2 vols. | or | H 1 | + | Cl 35.2 | = | HCl 36.2 |
| Hydrogen 1 vol. | + | Bromine 1 vol. | = | Hydrobromic Acid 2 vols. | or | H 1 | + | Br 79.4 | = | HBr 80.4 |
| Hydrogen 1 vol. | + | Iodine 1 vol. | = | Hydriodic Acid 2 vols. | or | H 1 | + | I 126 | = | HI 127 |
| Nitrogen 1 vol. | + | Oxygen 1 vol. | = | Nitrogen Dioxide 2 vols. | or | N 14 | + | O 16 | = | NO 30 |

It has further been found that the following compounds of two elements contain two volumes of one element and one volume of the other, but that these three volumes are condensed during the act of combination into two volumes:—

| | | | | | | | | | | |
|---------------------|---|-------------------|---|-------------------------------|----|-------------------|---|-------------------|---|----------------------------|
| Hydrogen 2 vols. | + | Oxygen 1 vol. | = | Steam 2 vols. | or | 2H 2 | + | O 16 | = | H_2O 18 |
| Hydrogen 2 vols. | + | Sulphur 1 vol. | = | Hydrogen Sulphide 2 vols. | or | 2H 2 | + | S 32 | = | H_2S 34 |
| Nitrogen 2 vols. | + | Oxygen 1 vol. | = | Nitrogen Monoxide 2 vols. | or | 2N 28 | + | O 16 | = | N_2O 44 |
| Nitrogen 1 vol. | + | Oxygen 2 vols. | = | Nitrogen Tetroxide 2 vols. | or | N 14 | + | 2O 32 | = | NO_2 46 |
| Sulphur 1 vol. | + | Oxygen 2 vols. | = | Sulphur Dioxide 2 vols. | or | S 32 | + | 2O 32 | = | SO_2 64 |

To this list must be added hydrogen selenide (H_2Se), hydrogen telluride (H_2Te), selenious oxide (SeO_2), and tellurous oxide (TeO_2).

Still a third mode of combination by volume, with condensation of four volumes to two, occurs in the two following cases:—



In all these cases, the *unit volume* is, of course, the same for every element and compound. What the absolute bulk of this unit volume may be, is not an essential point; for the relations remain the same, whatever the unit of measure. Three condensation ratios are thus exhibited,—first, a condensation of 0; second, one of $\frac{1}{3}$; and, third, one of $\frac{1}{2}$. The space occupied by the compound molecule is in each case exactly twice the unit volume:

The examples just given are only very few compared with the vast number of gaseous compounds which have been investigated, and where the same thing has been found to hold true. Two volumes of a compound gas invariably result from the chemical combination of one volume of hydrogen with one volume of chlorine, of two volumes of hydrogen with one volume of oxygen, of three volumes of hydrogen with one volume of nitrogen, and so on. This doubled volume is often called the *normal* or *product volume* of a compound gas.

If, in considering the compounds already mentioned in this chapter, we choose for our unit volume the space occupied by the atom of hydrogen in the molecule of hydrochloric acid (i.e., in other words, the volume of the atom of hydrogen when not under condensation), we shall be led to very important theoretical results; for then our product volume will be in each case the space occupied by the molecule of the compound gas, and we shall be led to the conclusion that the space occupied by a single molecule of each of these gaseous compounds is the same. This is, indeed, believed to be true in the case of all gaseous molecules. In organic chemistry a great multitude of compounds, many of them very complicated, has been investi-

gated, and the same law has been found to hold good. The molecule of every compound in the gaseous state occupies a volume twice as large as that occupied by the atom of hydrogen.

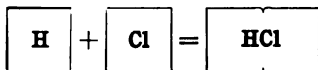
Since, then, the molecule of a compound gas occupies two of these unit volumes, and the vapor density (§ 39) of a gas is the weight of one unit volume of that gas as compared with the weight of the same volume of hydrogen, it is obvious that the vapor density of the gas may be found from the molecular weight by dividing the latter by two. *The vapor density of a compound gas is, therefore, one half its molecular weight.* This truth is one of great importance in its practical applications, since the chemist has only to determine by experiment the vapor density of a substance in order to obtain its molecular weight.

169. Molecular Condition of Elementary Gases. — Under the influence of heat, all *true gases* expand in the same proportion for the same increase in temperature (§ 19); further, all true gases comport themselves in the same way under the influence of an increase or decrease of pressure (§ 19). These facts are best explained by the hypothesis usually spoken of as the **Law of Avogadro**, that *equal volumes of all gases, under like conditions of temperature and pressure, contain the same number of molecules.*

This law is confirmed by certain facts relating to the diffusion of gases, and can be demonstrated to be true by a purely mathematical process of reasoning, if it be admitted that the mechanical theory of gases is true. Starting with this hypothesis, let us inquire what inferences may be drawn with regard to the molecular condition of the elementary gases when in the free state.

Suppose, then, we take any volume of hydrogen, the volume occupied by 1,000 molecules, for example: an equal volume of chlorine will contain the same number of molecules. If the two gases be mixed and exposed to diffused sunlight, they will combine without condensation to form hydrochloric acid. We shall then have two volumes of hydrochloric acid. According to the assumption just made, that equal volumes of all gases contain the same number of molecules, each of these two volumes will contain 1,000 molecules of the acid, and the two volumes will contain 2,000 molecules. Each molecule of the acid

contains one atom of hydrogen and one atom of chlorine, hence in the two volumes of hydrochloric acid we shall have 2,000 atoms of hydrogen and 2,000 atoms of chlorine. These 2,000 atoms of hydrogen (or chlorine) came from the volume of gas which we suppose to contain 1,000 molecules; therefore this volume contained at the same time 1,000 molecules and 2,000 atoms; hence each molecule must be made up of two atoms. It is clear that this train of reasoning is independent of the particular numerical value assumed as the number of molecules in the two volumes of hydrochloric acid. The fact of observation that the molecule of hydrochloric acid contains as small an amount of hydrogen as exists in any compound of this element, and as small an amount of chlorine as exists in any compound containing chlorine, permits us to believe that the molecule of HCl contains a single atom of hydrogen and a single atom of chlorine, as is represented by the formula, and by the diagram —



But by parity of reasoning we may assign to *free* hydrogen and *free* chlorine the formulas HH and ClCl , or H_2 and Cl_2 , and represent the constitution of all uncombined gases by such diagrams as —



Upon these models the molecular formulas of most of the elements with which we have become acquainted might readily be written. It is only in a *free* state that the elementary gases are thus conceived to exist as molecules: when they enter into combination, it is by atoms rather than by molecules. An atom of hydrogen unites with an atom of chlorine: three atoms of hydrogen combine with one of nitrogen.

In all cases when one volume of any element in a gaseous condition unites with one volume of another to form two volumes of a compound gas, it can be shown that the molecules of the two elements consist of two atoms. The number of atoms contained in the molecules of elements which form compounds that can be studied in the gaseous state, may be demonstrated by methods similar to those employed in the case of hydrogen. For example, mercury forms with chlorine a compound known as mercuric chloride, the molecule of which contains one atom of mercury and two atoms of chlorine, and is represented by the formula HgCl_2 . This substance contains as small an amount of mercury as is known to exist in any compound of this

element; but by the decomposition of two volumes of mercuric chloride, under suitable conditions as to temperature, there can be obtained two volumes of mercury in the gaseous condition, and two volumes of chlorine gas. If it be assumed that the two volumes of the substance decomposed contained 2,000 molecules of mercuric chloride, it follows from Avogadro's Law that there will be an equal number of molecules of mercury—that is to say, 2,000 molecules of mercury—in the two volumes of gaseous mercury which have resulted from the decomposition of the chloride. Moreover, there will be 2,000 molecules of chlorine in the two volumes of this gas. But, since the 2,000 molecules of mercury must necessarily contain all the atoms of mercury that were contained in the original 2,000 molecules of mercuric chloride, it appears that each molecule of mercury can contain only one atom, and that in the case of this particular element, which is evidently an exceptional case, the atom and the molecule are identical.

170. We may study the condition of the elementary gases from another point of view. If the Law of Avogadro be true of *all gases*, it will be true that the vapor density is one half of the molecular weight, and *vice versa*, that the molecular weight is twice the vapor density; for, as the vapor density of a body is determined by comparing the weight of a given volume thereof in the gaseous state with the weight of the same volume of hydrogen under the same conditions of temperature and pressure, it will then express the weight of the molecule in terms of the hydrogen molecule. The *unit of molecular weight*, however, is the same as the *unit of atomic weight*; namely, the weight of the *half hydrogen molecule*, or *hydrogen atom* and hence the *vapor density* must be doubled in order to express the weight of the molecule of the substance in terms of this unit. If, now, the vapor density of hydrogen be 1, its molecular weight must be $2 \times 1 = 2$. If the molecule weigh 2, and the atom weigh 1, the unit of weight being the same in both cases, the molecule must contain 2 atoms. The same reasoning will hold in the case of the elementary gases, oxygen, fluorine, chlorine, and nitrogen; also in the case of the elementary substances, bromine, iodine, sulphur, selenium, and tellurium, which are not gases under ordinary atmospheric conditions, but which can be converted into gases at a higher temperature. For example, taking the approximate vapor densities, we have—

| | Vapor Density. | Molec. Weight. = V. D. \times 2. | Atomic Wt. | No. of Atoms in Molecule. |
|------------|----------------|---------------------------------------|------------|------------------------------|
| O | 15.88 | 32 | 16 | 2 |
| Cl | 35.2 | 70.4 | 35.2 | 2 |
| I | 126 | 252 | 126 | 2 |
| S | 31.76 | 64 | 32 | 2 |

Of the other elementary substances, seven — arsenic, phosphorus, mercury, cadmium, zinc, sodium, and potassium — have been converted into gases, and their vapor densities have been determined. If we apply the same reasoning to these elements, we find that the molecules of arsenic and phosphorus contain each four atoms, while the molecules of mercury, cadmium, zinc, sodium, and potassium contain each a single atom only. For example:—

| | Vapor Density. | Molecular Weight. | Atomic Weight. | No. of Atoms in Molecule. |
|--------------|----------------|-------------------|----------------|---------------------------|
| As. | 148.8 | 297.6 | 74.4 | 4 |
| P | 61.6 | 123.2 | 30.8 | 4 |
| Hg | 99.25 | 198.5 | 198.5 | 1 |
| Cd. | 55.7 | 111.4 | 111.4 | 1 |

If this view of the molecular structure of the elements in the gaseous condition be correct, perfect consistency would require that no equation should ever be written in such a manner as to represent less than a single molecule of an element in a free state as either entering into or issuing from a chemical reaction. Thus, instead of —



it would be necessary to write —



We have not heretofore conformed to this theoretical rule, and do not propose to in the succeeding pages; and this for three reasons, — first, because many equations representing chemical reactions must be multiplied by 2 in order to bring them into conformity with this hypothesis concerning molecular structure, the equations thus being rendered unduly complex; secondly, because, in undertaking to make chemical equations express the molecular constitution of elements and compounds, as well as the equality of the atomic weights on each side of the sign of equality, there is imminent danger of taking the student away from the sure ground of fact and experimental demonstration, into an uncertain region of hypotheses based only on definitions and analogies; thirdly, because we are ignorant of even the probable molecular symbol of most of the elements. Of all the elementary substances recognized, we have reason to believe that ten, when in the gaseous state, are made up of molecules containing each two atoms, that two contain four atoms, and that five contain only a single atom to the molecule. Of the molecular structure of the remaining elements, numbering three fourths of the whole, we at present *know* nothing.

171. **Volumetric Interpretation of Symbols.** — We have already seen (§ 168) that all gaseous molecules are believed, under like con-

ditions, to occupy the same space: consequently the symbols for all molecules may be taken to represent equal volumes of the substances indicated; and by general agreement *the symbol of a molecule, when used to express volumetric relations, always stands for two volumes*. The symbols of the individual elements, as H, O, N, etc., we have already used to represent (1) an atom of the element, and (2) a certain number of parts, by weight, of the elementary substance; namely, that number of parts which is indicated by the atomic weight. The same symbol may be also used to denote a certain *volume* of the element in question, when that element is in the gaseous state. We have already used (§ 28 and often) the symbols H, O, N, and S to denote one volume of hydrogen, oxygen, nitrogen, and sulphur (gas) respectively and, in general, when the element is one whose molecule contains two atoms, the symbol for the atom is used to indicate one volume. In the exceptional case of the element being one whose molecule contains only one atom, the symbol for the atom will be also the symbol of the molecule, and will denote two volumes: thus Hg denotes two volumes of mercury vapor. When the element is one whose molecule contains four atoms, the symbol for the atom will indicate only half a volume: thus P stands for only half a volume of phosphorus vapor. As the great majority of the known elements cannot be volatilized, or made gaseous, by the highest temperatures as yet at our command, under conditions which permit the chemist to experiment with the gases produced, it is plain that the composition by weight is, in the present state of chemistry, of far greater practical importance than composition by volume.

172. Variation in the Number of Atoms in the Molecule of the Same Element.—It is not necessary to suppose that the molecules of the elementary substances invariably contain the same number of atoms. The molecule of sulphur at a temperature of 500° contains 6 atoms; its vapor density being about 96, and its molecular weight 192. While the simple compound of sulphur known as *hydrogen sulphide* has a vapor density of 17, and therefore a molecular weight of 34, 34 parts by weight of this compound contain very nearly 32 parts by weight of sulphur combined with 2 parts by weight of hydrogen. This is as small an amount of sulphur as exists in any known compound containing sulphur, therefore the atomic weight of sulphur cannot exceed 32: whence it follows that the molecule of sulphur at 500° must contain 6 atoms (or $192 \div 32$) of sulphur. On heating the gaseous sulphur to a higher temperature, it expands; and at 1200° its vapor density is about 32, and its molecular weight is about 64: hence the molecule at this temperature consists of 2 atoms. In the solid state, the molecule of sulphur may contain many more than 6 atoms. Selenium is similar to sulphur, the molecule undergoing like dissocia-

tion, and the vapor density decreasing with an increase of temperature. At a white heat, the molecules of phosphorus and of arsenic consist of 2 atoms instead of 4, the vapor density decreasing with the increase of temperature. So, too, at high temperatures, the molecules of iodine undergo dissociation, and consist of but one atom, as is probably the case also with bromine and chlorine. The phenomena of allotropism are best explained by supposing either that the various modifications have a different number of atoms in the molecule, or that there is some difference in the arrangement of these atoms. In the case of ozone there is good reason to suppose that the molecule contains 3 atoms, while the molecule of oxygen contains only 2, as has been already stated in § 123, and as will appear from the consideration of the vapor density and volumetric relations of the two substances. The vapor density of ozone is 24: its molecular weight is, then, 48; and, as the atomic weight of oxygen is 16, the molecule of ozone contains 3 atoms, while that of ordinary oxygen, which has a vapor density of 16, contains but 2. Again, when ozone is heated, it decomposes into ordinary oxygen, and every 2 volumes of ozone decomposed yield 3 volumes of oxygen. If we assume that 2 volumes of ozone contain 2,000 molecules, then, by Avogadro's Law, the 3 volumes of oxygen resulting must contain 3,000 molecules of oxygen; and, as each molecule of oxygen contains 2 atoms, we have 6,000 atoms of oxygen obtained from 2,000 molecules of ozone, each molecule of which must contain, therefore, 3 atoms. Selenium also appears to be triatomic in one form.

173. Atomic Weight and Specific Heat.—The determination of the atomic weights (§ 30) depends primarily upon the results of analysis. A careful analysis is made of as many compounds of the element as possible; and, on examining the results of these analyses, we select as the atomic weight the smallest proportional quantity which has been found to exist in any of the compounds, this proportional quantity being expressed in terms of the hydrogen atom as unity. Such a method can, however, only give results which represent either the atomic weight or some multiple thereof. In order to obtain the real atomic weight, it is necessary that the number of atoms of the element in the molecule of some one of the compounds analyzed shall be determined. By an application of Avogadro's Law we can determine the atomic weights of many elements (§ 30) which are themselves volatile, or that form gaseous compounds the volumetric composition of which can be determined. But many elements are not volatile under conditions admitting a determination of their vapor density, and do not form volatile compounds. Take, for example, the case of silver: an analysis of several compounds of this element gives us 107.1 as representing the proportion by weight in which silver enters into combination, for all compounds of this element

hitherto analyzed contain either 107.1 parts by weight or some multiple or submultiple thereof. It is possible that this figure may represent the weight of 1, 2, 3, or 4, etc., atoms, though it is agreed among chemists to accept 107.1 as representing the weight of one atom. Avogadro's Law is of no use in this case, since silver forms no compound which admits of its application.

There are certain methods, however, by which, in many cases, we can determine what multiples of the figures obtained by analysis should be used. By far the most important of these methods depends upon the relations which exist between the *specific heat* (§ 22) of the elements and the *atomic weights* as determined by analytical methods. When the solid elements are compared one with the other with reference to their specific heats, a comparatively simple relation is found to exist between the figures which represent the relative capacities for heat of the several elements, and the numbers which, from the results of analysis, etc., would naturally be regarded as the weights of their atoms. This relation is formulated in the **Law of Dulong and Petit**, that the *atomic weight is inversely proportional to the specific heat*. This law may be expressed in the following proportion:—

$$\left\{ \begin{array}{c} \text{Specific heat} \\ \text{of A} \end{array} \right\} : \left\{ \begin{array}{c} \text{Specific heat} \\ \text{of B} \end{array} \right\} = \left\{ \begin{array}{c} \text{Atomic weight} \\ \text{of B} \end{array} \right\} : \left\{ \begin{array}{c} \text{Atomic weight} \\ \text{of A} \end{array} \right\}.$$

It is true that practically the proportions are found to be only approximately correct, but the agreement is quite close enough to indicate a connection between the two sets of figures. Obviously, if this law is true, the product of the specific heat of any solid element by its atomic weight is a constant number. This constant is known as the *atomic heat*, and, taking the average of all the different values hitherto found, it may be expressed by the number 6.4. If we divide this number by the specific heat of an element, we shall obtain a number which approximately represents the atomic weight,—

$$\text{A.W.} = \frac{6.4}{\text{Sp.H.}}$$

Thus we are enabled to infer which of the figures obtained as the result of analysis should be adopted as the atomic weight. For example, in the case of platinum the results of analysis indicate that the atomic weight is 193.6, though, in so far as the analysis goes, these figures may just as well represent the weight of two atoms or of three or any other number of atoms. But the specific heat of platinum has been found to be 0.033; and on dividing the atomic heat, 6.4, by this quantity, we obtain the figures 193.9, which agree so closely with the supposed atomic weight as above given, that we are forced to conclude that the number 193.6 really represents the weight of one atom.

CHAPTER XII.

EMPIRICAL AND RATIONAL FORMULAS.

174. Empirical Formulas.—All formulas which express merely the number of atoms of each element in one molecule of a compound as determined by analysis are called *empirical*. The truth of such a formula depends solely upon the correct performance of the analytical process, and upon the accuracy with which the atomic weights have been determined. Concerning such formulas there is little room for difference of opinion: they express all that is actually known of the elementary composition of the compounds they represent.

175. Determination of Formulas.—If we know the percentage composition of a substance, and the atomic weights of the elements of which it is composed, it is a comparatively simple matter to calculate the *relative* number of atoms of each element in the molecule. But we cannot from these data be certain as to the precise number of atoms of each element, for there may be an infinite number of formulas corresponding to a given percentage composition. For example, take ammonia gas: ammonia contains in 100 parts by weight 82.353 parts of nitrogen and 17.647 parts of hydrogen; and these figures correspond not only to the formula NH_3 , but to any multiple of that formula, as can be shown by calculating the percentage composition of N_2H_6 , N_3H_9 , etc. Each of these formulas, of course, leads to the same result. In order to determine the true symbol of the molecule, we must know the molecular weight in addition to the percentage composition. When the molecular weight is known, the problem can be solved easily and definitely. Thus, in the example, if we know that the molecular weight of ammonia is 17, it is seen at once that the symbol must be NH_3 , and not some multiple thereof. Again, suppose it be desired to determine the symbol of alcohol. The analysis of pure alcohol expressed in percentages is as follows:—

| | |
|--------------------|--------|
| Carbon | 52.18 |
| Hydrogen | 13.04 |
| Oxygen | 34.78 |
| | <hr/> |
| | 100.00 |

Alcohol can easily be converted into a gas, and its vapor density has been found by experiment to be 23: the molecular weight is, then,

$$23 \times 2 = 46.$$

Since the elements will be present in the same relative proportions in 46 parts by weight as they are found to be in 100 parts by weight, we may state and solve the following proportions in order to determine the total weight of each element in the molecule:—

$$100 : 52.18 = 46 : x = 24, \text{ the weight of the total number of atoms of carbon.}$$

$$100 : 13.04 = 46 : x = 6, \text{ the weight of the total number of atoms of hydrogen.}$$

$$100 : 34.78 = 46 : x = 16, \text{ the weight of the total number of atoms of oxygen.}$$

The total weight of the atoms of each element divided by the atomic weight of that element will give the number of atoms of each in the molecule,—

$$24 \div 12 = 2 \text{ atoms of carbon.}$$

$$6 \div 1 = 6 \text{ atoms of hydrogen.}$$

$$16 \div 16 = 1 \text{ atom of oxygen.}$$

The empirical formula of the molecule of alcohol is, then, C_2H_6O . In an exactly similar manner the formulas of all compounds whose molecular weight can be determined may be obtained. (See note, p. 394a.)

In order to determine exactly the symbol of a compound, it is sufficient to know the approximate molecular weight. It is not essential to know this weight exactly, but only nearly enough to enable us to choose between a few multiples. When the substance is a gas, or if it can be converted into a gas without undergoing decomposition, a determination of the vapor density will of course give us the molecular weight. Thus the determination of the vapor density is oftentimes of great importance in enabling the chemist to determine the exact atomic composition of the molecule. There are many compounds of carbon especially, having exactly the same percentage composition, which differ widely as to their chemical and physical properties; and it is obvious that in connection with such substances a determination of the vapor density of each, and its true molecular weight, must be very important.

When on account of the nature of the substance it is not possible to determine its molecular weight, some conclusions can still frequently be drawn in regard to the matter, either from the chemical reactions of the body, or by comparing it with other similar substances the molecular weights of which are known. It is always practicable

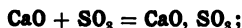
to find which one, among all possible formulas, expresses the composition of a substance most simply. For example, there is a compound of iron and oxygen which has the percentage composition, Fe, 70.01; O, 29.99; and it is known that the atomic weight of iron is 55.6, and that of oxygen 16.

Let us assume that the molecular weight of the compound is 100: then $70.01 \div 55.6 = 1.2574$, the number of atoms of iron in the molecule; and $29.99 \div 16 = 1.8744$, the number of atoms of oxygen in the molecule: for these figures would represent the number of atoms of iron and of oxygen in the molecule if the molecular weight were 100. This result is inadmissible, because fractions of atoms cannot exist. It will be seen at a glance, however, that the number of atoms which are possible must either be a multiple or submultiple of the numbers above given; and we can easily find the two smallest whole numbers which stand in the same relation to each other as 1.2574 and 1.8744, a proportion which is satisfied by the relation 2:3. Hence the *simplest possible formula* of the compound is Fe_2O_3 , though, for all that we know, the *actual* composition of the molecule may be represented by some multiple of the formula; namely, by $\text{Fe}_{2n}\text{O}_{3n}$. Similarly, in the case of other substances, we usually write the formula in the simplest possible form when we are unable to determine the molecular weight; so that in the case of such bodies the formula used may really be but a submultiple of the formula which would actually represent the number of atoms of each element in the molecule.

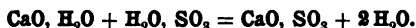
176. Rational Formulas. — Chemists have endeavored to contrive formulas which shall express something more than the mere elementary composition by weight, and the aggregates of the elements in the molecule. It is often highly convenient to be able to write out formulas which shall recall the materials from which the formulated substance was made, and prophesy the products of its decomposition, which shall not only name and number the atoms of the substance, but also suggest such a grouping or arrangement of those atoms as may serve to interpret its known reactions, and which shall even express the relations which subsist between the atoms composing the molecule, and show its probable structure. Such formulas are called *rational formulas*. It is evident that there may be various rational formulas for the same substance; in fact, for *acetic acid*, a compound of carbon, oxygen, and hydrogen, to be described in a subsequent chapter, no fewer than nineteen formulas have been proposed.

177. Dualistic Formulas. — One important class of rational formulas, formerly in common use, comprises those based on the view that the compounds they represent are *dual* in nature. Thus the oxygen acids, their salts and the metallic hydroxides, were at one time supposed to be made up of two oxides which were distinct before they were brought together to form the compound, and became distinct and

individual again when separately extracted from it. Formulas representing this conception of the constitution of bodies are called *dualistic*. Thus, for example, nitric acid (HNO_3) was written H_2O , N_2O_5 ; sulphuric acid, H_2O , SO_3 ; chloric acid, H_2O , Cl_2O_5 ; sulphurous acid, H_2O , SO_2 ; the salts were represented as containing an oxide of the metal (or *base*) and the acidic oxide (or *acid*). Thus, for example, sodium nitrate (NaNO_3) was written Na_2O , N_2O_5 ; sodium sulphate, Na_2O , SO_3 ; potassium chlorate, K_2O , Cl_2O_5 ; calcium sulphite, CaO , SO_2 . Similarly, the hydroxides were represented as containing an oxide of the metallic element and water. Thus sodium hydroxide (NaOH) was written Na_2O , H_2O ; calcium hydroxide, CaO , H_2O ; etc. The supposition upon which these formulas are based was not unnatural: thus, for example, common plaster of Paris is a substance containing the metal calcium and the elements sulphur and oxygen in the proportions by weight which are correctly expressed by the formula CaSO_4 ; but the substance known as *calcium sulphate* may be made by methods which suggest another formula. If we put together quicklime (CaO) and sulphuric anhydride (SO_3) in due proportions, under suitable conditions, we shall have a reaction which may be expressed by the equation



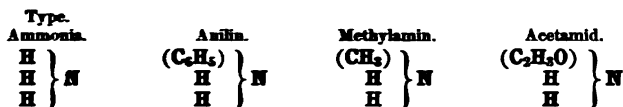
or if we mix slaked lime (CaO , H_2O) with sulphuric acid (H_2O , SO_3) in proper proportions, at a suitable temperature, we shall again obtain calcium sulphate, and water will be eliminated,—



Dualistic formulas are still much used in mineral chemistry.

178. **Typical Formulas.**—Another way of writing chemical formulas, now somewhat fallen into disuse, was in accordance with the so-called *doctrine of types*, which, in its simplest form, depended on the supposition that every possible chemical combination might be imagined to be built upon the plan, or framed upon the model, of some one of three substances; namely, hydrochloric acid (or free hydrogen), water, and ammonia, as in the examples:—

| | | | |
|--|--|---|---|
| Type. Hydrochloric acid. $\begin{array}{c} \text{H} \\ \text{Cl} \end{array} \}$ | Free hydrogen. $\begin{array}{c} \text{H} \\ \text{H} \end{array} \}$ | Sodium chloride. $\begin{array}{c} \text{Na} \\ \text{Cl} \end{array} \}$ | Methyl hydride. $\begin{array}{c} (\text{CH}_3) \\ \text{H} \end{array} \}$ |
| Type. Water. $\begin{array}{c} \text{H} \\ \text{H} \end{array} \} \text{O}$ | Sodium hydroxide. $\begin{array}{c} \text{Na} \\ \text{H} \end{array} \} \text{O}$ | Nitric acid. $\begin{array}{c} \text{NO}_2 \\ \text{H} \end{array} \} \text{O}$ | Alcohol. $\begin{array}{c} (\text{C}_2\text{H}_5) \\ \text{H} \end{array} \} \text{O}$ |



It will be noticed in these examples that the hydrogen of the type may be replaced, not only by a single atom, but also by a group of atoms; that is, by a compound radical (§ 75).

179. Structural or Graphic Formulas.—Another system of rational symbols now in almost universal use among chemists is based upon the doctrine of *valence* (§ 85), according to which every atom has the power of fixing or combining with a certain definite number of other atoms. In order to obtain a measure and a mode of expressing the combining powers of atoms, pains have been taken to determine for each element how many atoms of hydrogen (or other element that can be substituted for hydrogen) the atom can unite with. From these researches it has appeared that the atom-fixing power, or valence, is not invariable, but that it varies according to circumstances; for instance, it may sometimes vary with the temperature. Thus, phosphorus has a valence of five towards chlorine at ordinary temperatures, as is shown by the compound PCl_5 ; but at a high temperature it has a valence of only three towards the same element, as is shown by the fact that phosphorus pentachloride, when heated, is dissociated into a molecule of the composition PCl_3 and a molecule of chlorine. Again, the valence of an element often varies with the chemical character of the elements with which it combines. Nitrogen is trivalent towards hydrogen, as in ammonia (NH_3), but is capable of forming a compound containing one atom of chlorine and four atoms of hydrogen, in which it exerts a valence of five. Similarly, chlorine, while capable of combining with but one atom of hydrogen to form hydrochloric acid, can form compounds containing both hydrogen and oxygen, in which it probably exerts an atom-fixing power of seven. It appears, in fact, that *the valence of an elementary atom is not an invariable property of the atom*, but that each of the observed differences as to its valence is an invariable property of some particular condition of the atom dependent on the circumstances in which it is

placed. Chlorine is always univalent in hydrochloric acid, and nitrogen is always trivalent in ammonia.

180. In writing formulas in accordance with the foregoing hypothesis, it is customary to draw lines or bonds between the several atoms, — one line in case the compound consists of two univalent elements, as in hydrochloric acid, $\text{H}-\text{Cl}$; two lines if there is union between a bivalent atom and two univalent atoms, as in water, $\text{H}-\text{O}-\text{H}$ or $\text{O} < \text{H}$; three lines when a trivalent element like nitrogen holds

three univalent atoms in combination, as in ammonia, $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{N}-\text{H} \end{array}$ or $\begin{array}{c} \text{H} \\ / \\ \text{N}-\text{H} \\ \backslash \\ \text{H} \end{array}$. Marsh gas (CH_4), in which carbon acts as a quadrivalent ele-

ment, may be written $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$; while ammonium chloride (NH_4Cl),

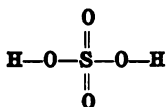
in which nitrogen has a valence of five, may be written $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{N}-\text{H} \\ / \quad \backslash \\ \text{Cl} \quad \text{H} \end{array}$.

According to this theory, no molecule can exist the atoms of which could be represented by bonds unconnected with other atoms. Thus there could be no such molecule as OH ; for if written graphically, $-\text{O}-\text{H}$, it is seen that the oxygen atom would be left unsatisfied. Many groups of atoms (such as OH), which contain unsatisfied polyvalent elements, are capable of acting collectively as if they were single atoms: they are the so-called *compound radicals*, and play highly important parts in a multitude of reactions. The valence of such a group is determined in each case by the number of unsatisfied bonds. Thus the group $(\text{OH})-$, known as *hydroxyl*, is a univalent radical, while $\text{H}-\text{O}-\text{H}$ (water) and $\text{H}-\text{O}-\text{OH}$ (hydrogen dioxide) are *saturated molecules*.

There are, moreover, many substances capable of existing separately, which under certain conditions can combine with other substances, while the valence of some atom or atoms in the molecule is increased. Thus, as was just now said, in ammonia gas (NH_3) the atom of nitrogen is trivalent; but, when ammonia reacts with hydrochloric acid (HCl), a valence of five is exerted by the nitrogen atom, and ammonium chloride is formed by the addition of two univalent atoms to the molecule. Bodies which can thus form *addition products* are said to be *unsaturated*.

181. It should be clearly understood that the grouping of atoms in *structural* or *graphic* formulas is not an arbitrary matter, of the nature

of a dissected map. In the arrangement of the atoms it is not simply a question of so linking them together that the conditions implied by their valence shall be satisfied; such formulas attempt also to represent in some sense the *structure of the molecule*, at least in so far as to indicate the relations which we believe to exist among the various atoms which compose it. As an illustration of this idea, we may take the structural formula of sulphuric acid, which is usually written —



The existence of the oxide SO_3 , and of normal sulphuric acid, $\text{S}(\text{OH})_6$ (often spoken of as a hydrate, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$), leads to the belief that the atom of sulphur in the acid is hexavalent; and the formula as printed is the only one which will represent this view and satisfy its requirements. In this formula, the sulphur, by virtue of its hexivalence, holds the other atoms in combination. Two of the oxygen atoms are associated only with the sulphur atom, and the combining powers of these two bivalent atoms are wholly exerted in holding them to the atom of sulphur. The two dashes indicate, that, when an oxygen atom is combined with only one other atom, two degrees of valence are exerted. Although we have little evidence of what the actual relation between atoms thus conventionally represented as acting upon each other really is, it is found, that, if oxygen or another bivalent atom thus combined is replaced by univalent atoms, two of them are required to take its place and saturate the molecule. Indeed, when atoms are thus represented as united by the two dashes, or double bond, the fact actually indicated is, that, if replacement is brought about, it must be by a single bivalent atom (or group), or else by two univalent atoms (or groups of atoms). It will be noticed that the formula indicates the existence of two hydroxyl groups in the molecule. Now, when sulphuric acid is treated with phosphorus trichloride (PCl_3), a reaction occurs which may be written as follows:—



and when written graphically, HClSO_3 is $\text{H}-\text{O}-\text{S}-\text{Cl}$, which shows

$$\begin{array}{c} \text{O} \\ || \\ \text{H}-\text{O}-\text{S}-\text{Cl} \\ || \\ \text{O} \end{array}$$

that one of the hydroxyl groups in sulphuric acid has been replaced by an atom of chlorine. But, on treating this substance in its turn with phosphorus trichloride, another reaction occurs; viz., —



and when written graphically, Cl_2SO_3 is $\text{Cl}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{S}-\text{Cl}$, whereby the

relations of this chloride to sulphuric acid are made manifest, and the correctness of the formula of that substance is proved; for in these formulas the two hydroxyl groups are seen to bear the same relation to each other and to the rest of the molecule. No matter whether one or the other of these groups is replaced by another atom or group of atoms, the same product would result; in fact, experiments show that there is only one substance having the composition represented by the formula HClSO_3 , while the existence of two bodies of this composition would be expected if there were any difference in the relations of the hydroxyl groups. There are other grounds for the correctness of the formula which might be urged if space permitted.

The great value of graphic formulas as a means of enabling the student to grasp complex relations will be seen on reflecting how little help of this sort is to be got in the present instance from the mere empirical formulas. On contrasting the formulas H_2SO_4 and HClSO_3 , it will appear only that a single *univalent atom* of chlorine seems to have replaced a *bivalent atom* of oxygen, and *one atom of hydrogen also*; while, on considering the matter in the light of the valence theory, it will be seen at once that the observed result can only take place when the oxygen and the hydrogen stand to one another in the relations indicated in the graphic formula.

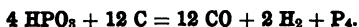
It is in respect to compounds of carbon that structural formulas have hitherto found their most important applications, as will be seen in the chapters relating to carbon. It should be borne in mind, however, that such formulas are in no sense intended to indicate the *spacial relations* of the atoms, but merely the manner in which the combining forces are exerted.

CHAPTER XIII.

PHOSPHORUS (P).—ATOMIC WEIGHT, 30.8.

182. **Phosphorus** occurs somewhat abundantly and very widely diffused in nature. It is never found in the free state, but almost always in combination with oxygen and some one of the metals. The most abundant of its compounds is *calcium phosphate*, which occurs as a native mineral, and

which also forms the mass of the mineral constituents of the bones of animals. From the small amounts of phosphates contained in ordinary soils, growing plants collect what they need; herbivorous animals, in their turn, consume the phosphorus compounds which have been accumulated by the plants; and from the bones of animals phosphoric acid and phosphorus can be prepared. On heating a mixture of phosphoric acid (H_3PO_4) and carbon to bright redness in a retort made of refractory clay, metaphosphoric acid, HPO_3 (§ 191) is reduced, and phosphorus distills over, as represented in the equation —



183. Phosphorus, when perfectly pure, is a transparent, colorless, wax-like solid of 1.8 specific gravity, which, when freshly cut, emits an odor like garlic; though under ordinary conditions this odor is overpowered by the odor of ozone, which, as has been previously stated (§ 121), is developed when phosphorus is exposed to the air. It unites with oxygen readily, even at the ordinary temperature of the air, and with great energy at somewhat higher temperatures (above 60°).

When in contact with air, it is all the while undergoing slow combustion; and, if the temperature of the slowly burning phosphorus be slightly increased in any way, the mass will burst into flame and be rapidly consumed. On account of this extreme inflammability, phosphorus must always be kept under water. It is best also to cut it under water, lest it become heated to the kindling point by the warmth of the hand, or by friction against the knife; for, when once on fire, it is exceedingly difficult to extinguish it, and, in case it happens to burn upon the flesh, painful wounds are inflicted, which are very difficult to heal.

On account of this easy inflammability by friction, phosphorus is extensively employed for making matches. The matter upon the end of an ordinary friction match usually contains a little phosphorus, together with some substance capable of supplying oxygen, such as red lead, black oxide of manganese, saltpeter, or potassium chlorate. The phosphorus and the oxidizing agent are kneaded into a paste made of glue or gum; and the wooden match sticks, the ends of which have previously been dipped in melted sulphur, are touched to the

surface of the phosphorized paste, so that the sulphured points shall receive a coating of it. The sulphur serves merely as a kindling material, which, as it were, passes along the fire from the phosphorus to the wood. By rubbing the dried, coated point of the match against a rough surface, heat enough is developed to bring about chemical action between the phosphorus and the oxygen of the other ingredient, combustion ensues, the sulphur becomes hot enough to take on oxygen from the air, and finally the wood is involved in the play of chemical force. Sometimes sulphur is not used; but, before applying the phosphorus mixture, the points of the matches are charred slightly, and touched to melted paraffin, in order that they may inflame readily.

Exp. 82. — Put a clean, freshly cut piece of phosphorus as big as a grain of wheat upon a piece of filter paper, and sprinkle over it some lampblack or powdered boneblack. The phosphorus will melt after a time, and will finally take fire. As stated above, phosphorus, when exposed to the air, is all the time undergoing slow combustion. This action is attended by evolution of heat. Both the lampblack and the paper are bad conductors of heat, and serve to prevent the phosphorus from losing that developed by the oxidation. Moreover, as will be explained more fully hereafter under carbon, the vapor of phosphorus which rises continually is absorbed by or dragged into the pores of the boneblack, and brought into intimate contact with oxygen which is or has been absorbed from the air. Chemical action ensues between the phosphorus vapor and the oxygen gas; and, as the heat which is generated is retained, the phosphorus ultimately takes fire.

184. At the ordinary temperature of the air, and still more at higher temperatures, phosphorus shines in the dark with a greenish white light; hence the name *phosphorus*, from Greek words signifying "light-bearing." This *phosphorescence* is seen when an ordinary friction match is rubbed against any surface in a dark room.

185. In warm weather, phosphorus is soft and somewhat flexible, and may then be bent without breaking. It melts at 44°, forming a viscid oily liquid, which boils at about 290°, and is converted into colorless vapor. Phosphorus can readily be distilled in a retort filled with some inert gas, like hydrogen, nitrogen, or carbonic acid. By the action of light it becomes yellow, and is coated with a nontransparent reddish white layer. When heated to about 230° out of contact with the air, phosphorus is converted into an allotropic modification known as *red phosphorus*.

Phosphorus is insoluble in water, but is somewhat soluble in ether, petroleum, benzol, oil of turpentine and other oils: it also dissolves abundantly in carbon disulphide.

If a solution of phosphorus in carbon disulphide be poured upon a sheet of filter paper, the carbon disulphide will soon evaporate, leaving the phosphorus in a very finely divided state. The phosphorus begins immediately to oxidize, and, as the paper is a bad conductor of heat, it presently will burst into flame. The paper, however, is not completely consumed, but a very considerable residue of carbon remains unburned. This depends upon the fact that the product of the combustion of the phosphorus, phosphoric oxide, quickly covers the paper with a varnish which is not only incombustible in itself, but is quite impervious to air.

Ordinary phosphorus is exceedingly poisonous. It is the effective agent in many of the common preparations which are employed for destroying rats and mice, cockroaches, ants, etc.

186. Red Phosphorus. — This remarkable allotropic modification of phosphorus is a body as unlike ordinary phosphorus in most respects as could well be conceived. It is a reddish brown powder, and has neither odor nor taste; it is not poisonous so far as is known, is not phosphorescent, does not take fire at ordinary temperatures, is insoluble in carbon disulphide, and in general behaves altogether differently from the ordinary modification. It is easy, however, to convert one variety into the other. If ordinary phosphorus be heated to 230° out of contact with the air, the red variety is formed; if this be heated still further to 260° , it changes back into the ordinary variety.

Exp. 83. — In a narrow glass tube (No. 6), about 30 cm. long and closed at one end, place a quantity of red phosphorus as large as a small pea; heat the phosphorus gently over the gas lamp, and note that a sublimate of a light-colored substance is quickly deposited upon the cold walls of the tube a short distance above the heated portion. This light-colored sublimate is ordinary phosphorus, as may be shown by cutting off the tube just below the sublimate, after the glass has been allowed to cool, and then scratching the coating with a piece of wire: the coating will take fire. The air in the narrow tube employed is deprived of its oxygen by the combustion of a small portion of the phosphorus at the moment of its transformation from the red to the ordinary condition: the remaining phosphorus is thus enveloped in nitrogen, and so protected from further loss.

Red phosphorus is employed to a certain extent as an adjunct to the so-called *safety matches*. Such matches contain no phosphorus in themselves, and will not take fire readily by friction upon an ordinary rough surface, though they burst into flame at once when rubbed upon a surface specially prepared with red phosphorus. The matter upon the tips of safety matches is usually a mixture of potassium chlorate and antimony sulphide, made into a paste by means of glue. The surface upon which the match is to be rubbed is composed of red phosphorus, black oxide of manganese, and glue. In favor of the use of red phosphorus for matches are the facts, that, unlike ordinary phosphorus, it is not deleterious to the workmen who have to deal with it, and it is far less liable to be set on fire by accidental friction.

A third modification of phosphorus is obtained if the amorphous variety be heated in a glass tube, free from air, to 530° , when microscopic black metallic crystals are deposited in the upper, cooler portions of the tube.

187. Phosphorus combines readily with many other elements beside oxygen. The ordinary modification of phosphorus combines violently with sulphur at temperatures near the melting point of sulphur, the act of combination being attended with vivid combustion and loud explosion. With chlorine, bromine, and iodine, ordinary phosphorus unites directly at the ordinary temperature of the air, the combination being rapid and attended with inflammation. Phosphorus unites directly with most of the metals to form *phosphides*.

188. **Compounds of Phosphorus and Hydrogen.** — There are three compounds of phosphorus and hydrogen, of which, at ordinary temperatures, one is gaseous (PH_3), one liquid (PH_4), and one solid (P_2H). The gaseous compound, or rather the gaseous compound charged with the vapor of the liquid compound, is somewhat interesting, from the fact that it takes fire spontaneously, immediately on coming into contact with the air.

Exp. 84. — In a thin-bottomed flask of about 140 cc. capacity put 1 g. of phosphorus and 115 cc. of sodium hydroxide, obtained by dissolving 40 g. of common caustic soda in 110 cc. of water. Pour two or three drops of ether upon the liquid in the neck of the flask, then close the flask with a cork carrying a long delivery tube of glass (No. 5). Place the flask over the gas lamp, upon the wire-gauze ring of the iron stand, and immerse the end of the delivery tube in the water pan, then gently heat the flask. The ether is added

to the contents of the flask, in order that the last traces of air may be expelled from the flask by the vapor which arises from this highly volatile liquid as soon as it is warmed.

As the solution becomes hot, small bubbles of gas will be seen

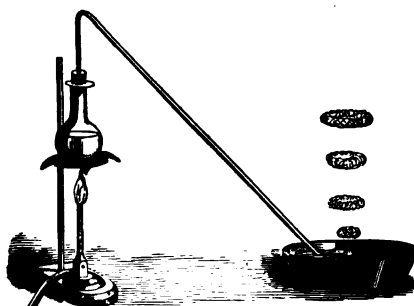
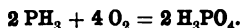


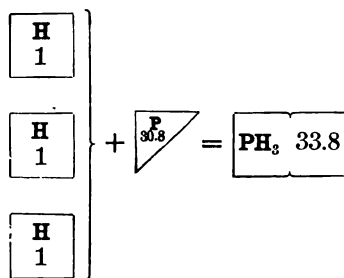
Fig. 37.

to arise from the surface of the phosphorus, and in a short time large bubbles of gas will escape from the delivery tube. Each of these bubbles, as it comes in contact with the air at the surface of the water, will spontaneously burst into flame, and burn with a vivid light and the formation of beautiful rings of white smoke, if the air be not disturbed by draughts.

In burning, the hydrogen phosphide is converted into phosphoric acid; and of this product the white smoke is, of course, composed, —



The atomic weight of phosphorus is 30.8; the specific gravity of its vapor has been found by experiment to be 61.6. In this respect phosphorus differs from the elements already studied, where the combining weights and the unit-volume weights have been identical. It follows, that, if the molecule of hydrogen contains two atoms of hydrogen, the molecule of phosphorus will contain four atoms of phosphorus (§ 170): the symbol of the molecule, then, is P_4 . If we compare the formula of hydrogen phosphide (PH_3) with that of ammonia (NH_3),



we see that the atom of phosphorus, which weighs 30.8, combines with the same quantity of hydrogen by weight as the atom of nitrogen; but while from two volumes of ammonia gas we may set free three volumes of hydrogen and one volume of nitrogen, from two volumes of hydrogen phosphide we get three volumes of hydrogen and only half a volume of phosphorus

vapor. The composition of hydrogen phosphide may thus be represented by the accompanying diagram.

Hydrogen phosphide, or **phosphine**, is colorless, and has a disagreeable garlic-like odor. Like ammonia, it combines with the halogen acids to form compounds, PH_4Cl , PH_4Br , PH_4I , in which the group PH_4 (phosphonium) plays the same part as the ammonium group in the ammonium compounds.

189. Oxides of Phosphorus. — There are three *oxides of phosphorus* answering to the formulas P_2O , P_2O_3 , P_2O_5 .

Hypophosphorous Oxide (P_2O). — When ordinary phosphorus is burned in a confined volume of air or oxygen insufficient for its complete combustion, there will be found admixed with the unconsumed phosphorus, after the chemical action has ceased, a certain quantity of a reddish brown powder, which is the oxide in question. An acid, *hypophosphorous acid* (H_3PO_2), corresponding to the oxide, is known; as are also the corresponding salts, the *hypophosphites*, of certain metals. Calcium hypophosphite, for instance, is $\text{Ca}(\text{H}_2\text{PO}_2)_2$. Since only one atom of hydrogen in hypophosphorous acid (H_3PO_2) is replaceable, it must be classed as a monobasic acid (§ 70). In the preparation of phosphine (Exp. 84) some sodium hypophosphite is formed, the reaction being —



Phosphorus trioxide or phosphorous oxide (P_2O_3). is formed by burning phosphorus with a limited supply of air. It is a white amorphous substance, very soluble in water, and burning in the air to phosphorus pentoxide (P_2O_5). Phosphorus trioxide reacts with water in accordance with the equation —



forming phosphorous acid, of which it thus appears to be the anhydride. It is often called *phosphorous anhydride*. The salts of this acid, known as the phosphites, are quite numerous.

190. Phosphorus Pentoxide, Phosphoric Oxide, or Phosphoric Anhydride (P_2O_5). — This oxide of phosphorus is the product of the rapid combustion of phosphorus in an excess of air or oxygen.

Exp. 85. — Dry thoroughly a large porcelain plate, a small porcelain capsule, and a wide-mouthed bottle of 2 l. capacity, by warming them. Place the capsule upon the plate, and put in the capsule a bit of dry phosphorus, of the weight of about half a gram; light the phosphorus, and cover it at once with the inverted bottle. The phosphoric anhydride formed by



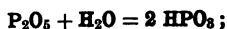
Fig. 38.

the combustion of the phosphorus will be deposited as a white powder, like flakes of snow, upon the sides of the bottle, and much of it will fall down upon the plate below.

The flocculent, amorphous, odorless powder thus obtained, unites with water with remarkable facility. If it be left in the air for a few minutes, it deliquesces completely. Upon being thrown into water, it dissolves with a hissing noise and development of much heat. This power to combine with water is its most marked property. In order to preserve it, it must be placed in a dry tube, and the tube closed by sealing it in the lamp.

In many operations in the "dry way," this oxide of phosphorus may act at high temperatures as a powerful acid to decompose minerals and other compounds which contain volatile constituents: hence it is often called *phosphoric acid* by chemists who are habitually occupied with such reactions.

191. **Phosphoric Acids.** — By the union of phosphoric anhydride with water, there are formed three distinct acids: *metaphosphoric acid* (HPO_3),



pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$),



and *ordinary orthophosphoric* or *tribasic phosphoric acid* (H_3PO_4),



Corresponding to these three varieties of phosphoric acid, there are three series of *phosphates*; viz., the *metaphosphates*, the *pyrophosphates*, and the *ordinary* or *ortho phosphates*.

Phosphoric acid (H_3PO_4), or **orthophosphoric acid**, as it is termed to distinguish it from other varieties, is produced when the pentoxide dissolves in hot water. It is the final product of the oxidation of phosphorus, and may be obtained by boiling phosphorus with nitric acid. When the aqueous solution is evaporated to dryness, the acid may be obtained in the form of colorless prismatic crystals, which are very deliquescent. The occurrence of compounds of this acid in nature has already been referred to in connection with the description of phosphorus, the principal compound being calcium phosphate.

The ordinary phosphates are all salts of this acid. Orthophosphoric acid is tribasic, being capable of forming three series of salts, — *primary* (as KH_2PO_4), *secondary* (K_2HPO_4), and *tertiary* (K_3PO_4), — according as one, two, or three atoms of hydrogen are replaced by metallic atoms. These salts are often named according to the hydrogen atoms replaced, as *monopotassium phosphate*, *dipotassium phosphate*, and *tripotassium phosphate*. In the salts of phosphoric acid it is not necessary that the hydrogen atoms should all be replaced by the same element. There are phosphates in which the hydrogen atoms are replaced by different bodies, forming *double salts*, such as ammonium magnesium phosphate (NH_4MgPO_4), and sodium ammonium phosphate ($\text{NaNH}_4\text{HPO}_4$), known as *microcosmic salt*. The common phosphate of soda is disodium phosphate (Na_2HPO_4).

Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) may be obtained by heating orthophosphoric acid to 200° – 300° . It may be regarded as formed by the removal of one molecule of water from two molecules of the common acid, —

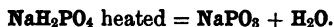


The acid is tetrabasic, forming numerous salts called *pyrophosphates*. Any secondary orthophosphate is changed into a pyrophosphate by heat.

Metaphosphoric acid (HPO_3) results on heating either the ortho- or the pyro-acid to 400° , or it may be formed by dissolving the pentoxide in cold water. It is a glassy, transparent substance, known commercially as *glacial phosphoric acid*. Metaphosphoric acid is a monobasic acid, like nitric acid, being capable of forming only one series of salts. It may be regarded as formed by the removal of one molecule of water from orthophosphoric acid, —



In general, the primary orthophosphates are converted into metaphosphates by heating, —



In the case of these phosphoric acids, the empirical formulas express all that is *known* of their composition, though there are some reasons for believing that their replaceable hydrogen atoms are in the hydroxyl condition.

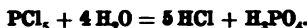
192. Halides of Phosphorus. — Phosphorus forms compounds with the halogens, in which the atoms of phosphorus are both trivalent and pentavalent. Of these compounds we need only consider the two chlorides. Phosphorus and chlorine unite readily and directly, even at low temperatures, the combination being attended with evolution of light and heat (Exp. 48, § 97).

Phosphorus trichloride, or phosphorous chloride (PCl_3), may be prepared by passing dry chlorine over gently heated phosphorus, when the trichloride distills over, and may be collected in a receiver. It is a colorless liquid readily decomposed by water into phosphorous and hydrochloric acids, —

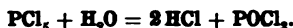


This reaction is a good illustration of the general property of the chlorides of acid-forming elements to react with water and form the corresponding hydroxides and hydrochloric acid. The vapor density of the trichloride has been determined experimentally as 68.2, which corresponds to the formula PCl_3 .

Phosphorus pentachloride, or phosphoric chloride (PCl_5), is produced by the action of an excess of chlorine on phosphorus or upon the trichloride. It is a solid crystalline substance which is readily decomposed by water. By a large excess of water it is immediately converted into hydrochloric and phosphoric acids, —

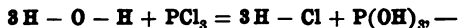
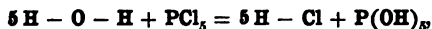


With a smaller quantity it yields hydrochloric acid and phosphoric oxychloride, —



On being heated, phosphorus pentachloride sublimes without fusing; meanwhile it is *dissociated* into the trichloride and chlorine. This decomposition, though gradual, is constant and definite in amount at any given temperature. On account of the decomposition, neither the vapor density nor the molecular weight of the pentachloride can be determined.

If we consider the reactions of the chlorides of phosphorus with water thus, —



it will be seen that the effect is a replacement of the hydroxyl group (OH) by chlorine; i.e., the groups of atoms we call hydroxyl, and the atoms of chlorine change places.

Similarly, when any compound which contains this group of atoms is treated with a chloride of phosphorus under proper conditions,

the same reaction takes place, the hydroxyl being replaced by chlorine. The chlorides of phosphorus are often used as a test for the presence of hydroxyl in compounds. If, on treating a compound containing hydrogen and oxygen with a chloride of phosphorus, an atom of chlorine replaces an atom of hydrogen *and* an atom of oxygen, we conclude that they are in the form of hydroxyl. This action of the chlorides of phosphorus upon hydroxyl compounds is well illustrated in the case of alcohol, the following reaction taking place:—



193. Phosphorus combines with sulphur to form a variety of bodies, among which are the trisulphide P_2S_3 , and the pentasulphide P_2S_5 , corresponding to the oxides P_2O_3 and P_2O_5 .

CHAPTER XIV.

ARSENIC, ANTIMONY, AND BISMUTH.

ARSENIC (As.) — ATOMIC WEIGHT, 74.4.

194. In small quantity, arsenic is very widely distributed in nature. Compounds of it have been known from very early times. It is sometimes found free in the metallic state, but generally in combination with oxygen or sulphur and some one of the metals, such as iron, cobalt, nickel, and copper.

195. Arsenic is a brittle solid of a steel-gray color and metallic luster. At a dull-red heat it may be converted into a vapor which has a peculiar garlic odor. Heated in the air or in oxygen, arsenic burns with a whitish flame, producing the white arsenic trioxide (arsenious oxide). Arsenic combines readily with chlorine, bromine, iodine, and sulphur; it also unites by fusion with most metals, forming alloys, which the arsenic tends to make hard or brittle. In the manufacture of shot, a little arsenic is added to the lead to facilitate the formation of regular globules.

As is the case with phosphorus, the vapor density of arsenic is double its atomic weight, and consequently its molecular symbol is As_2 .

196. **Hydrogen arsenide**, or **arsine**, often called **arseniuretted hydrogen** (AsH_3), is a colorless gas, having a fetid odor. Even when very much diluted with air, it is intensely poisonous, and fatal results have repeatedly followed its accidental inhalation. The gas may be prepared in an impure state mixed with hydrogen by introducing a solution of some compound of arsenic into a generator in which hydrogen is being produced from zinc and a dilute acid.

Hydrogen arsenide burns in the air with a whitish flame, forming water and a white smoke of arsenic trioxide; but if a cold body, like a piece of porcelain, for example, be introduced into a jet of the burning gas, the hydrogen alone will burn, and the arsenic will be deposited in the metallic state upon the porcelain surface, forming a lustrous black spot.

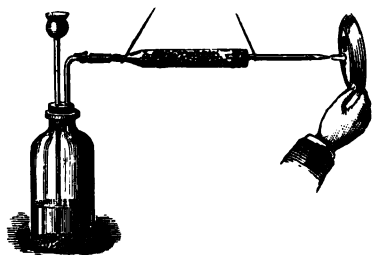


Fig. 39.

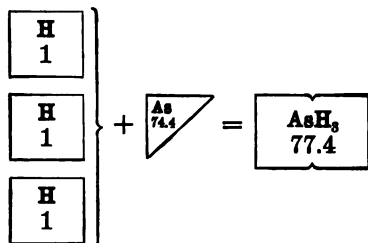
This effect is precisely similar to the deposition of soot on a cold body held in the flame of a candle. The gas is also decomposed when caused to pass through tubes heated to dull redness, metallic arsenic being deposited as a brown or blackish mirror, while hydrogen gas

escapes. These properties of hydrogen arsenide are made use of in testing for the presence of arsenic in cases of suspected poisoning.

Exp. 86.— Arrange a hydrogen generator as in Fig. 39, except that the delivery tube beyond the calcium chloride tube should be twice or three times as long as there represented, and should be drawn down to a narrow bore in several places. Generate hydrogen from zinc and dilute hydrochloric acid, and, when the whole apparatus is full of hydrogen, light the jet. Pour into the generator through the thistle tube a *few drops* of a solution of arsenic trioxide in hydrochloric acid. Watch the flame to see whether it appears to alter in character. Hold a concave piece of cold porcelain in the flame. A brownish black deposit of arsenic is formed. Collect several of these spots, and reserve them for a future experiment. While the stream of arseniuretted hydrogen is passing through the delivery tube, heat the

tube with the flame of a Bunsen lamp, a little behind one of the constricted portions. The arsine is decomposed, and arsenic is deposited in the tube as a metallic mirror. Produce several of these mirrors and save them, and then wash out the generator, zinc and all. This method of procedure is known as **Marsh's test**. *This experiment should only be performed where there is a good draught of air, owing to the exceedingly poisonous character of the gas; and the jet of gas must be kept constantly burning, in order to prevent the possibility of any of it escaping into the air of the room.*

The vapor density of arsine determined by experiment is 39,—a fact which makes it certain that two volumes of the gas do not contain one volume of arsenic gas, which has a density of about 150, but only half a volume, the gas having the same composition as phosphine, as represented in the following diagram:—



197. Compounds of Arsenic and Oxygen.—There are two well-defined oxides of arsenic,—*arsenic trioxide* or *arsenious oxide* (As_2O_3), and *arsenic pentoxide* or *arsenic oxide* (As_2O_5).

198. Arsenic trioxide or arsenious oxide (As_2O_3), often called *arsenious acid* or *white arsenic*, is formed when metallic arsenic or arsenical ores are heated in the air. It ordinarily occurs in small octahedral crystals, but is also obtained in vitreous amorphous masses. The two varieties differ from each other in several respects. The occurrence, thus, of one and the same chemical compound in forms differing in physical and chemical properties, while the fundamental chemical identity is retained, is said to be due to *isomerism* (§ 287). When heated with free access of air, arsenious oxide volatilizes without change: if heated in contact with carbon, it gives up its oxygen, and metallic arsenic is liberated. Arsenious oxide is somewhat

soluble in water. It dissolves readily in hot hydrochloric acid ; but, when the solution cools, most of the arsenious oxide is deposited unchanged.

Exp. 87. — Place a few particles of arsenious oxide in an open tube of hard glass (No. 5) about 10 cm. long, and heat it at the lamp by holding the tube in a sloping position. The white solid will be volatilized, but it will immediately be deposited again upon the cold part of the tube. By the aid of a lens, this deposit may be seen to be crystalline.

Exp. 88. — Drop into the point of a drawn-out tube of hard glass (No. 5) a morsel of arsenious oxide, and above it place a splinter of charcoal (Fig. 40); heat the coal red-hot in the flame of the lamp, and then volatilize the arsenious oxide. The oxide will give its oxygen to the coal, and the arsenic will be deposited in a ring on the cold part of the tube, presenting a brilliant metallic appearance.

Exp. 89. — Throw a minute particle of arsenious oxide upon a piece of red-hot charcoal. The oxide will be partly reduced, and the peculiar garlic odor of the vapor of metallic arsenic will be perceived.

199. Arsenious oxide is a violent poison, all the more dangerous because it has neither taste nor odor to warn the victim of its presence. Two decigrams of it will cause death.

Arsenious oxide is largely used in the manufacture of two well-known green pigments, — one an arsenite of copper, and one a compound of arsenite and acetate of copper. It is applied as an oxidizing agent in the manufacture of glass ; it is consumed in considerable quantities for poisoning vermin, and for producing the arsenical compounds used in the preparation of dyes ; it is used also in very small doses as a remedy for asthma, and in some skin diseases.

The trioxide dissolves with difficulty in water, the solution having a feebly acid reaction. On boiling a solution of arsenious acid together with strong hydrochloric acid, arsenic trichloride will be formed. From this fact, supported as it is by the other fact that the acid properties of the oxide are but feeble, it appears that arsenious oxide has basic characteristics, and that in this respect the oxide consists with the somewhat metallic nature of the element itself.



Fig. 40.

Arsenious acid (H_3AsO_3), of which the trioxide is regarded as the anhydride, and hence often termed *arsenious anhydride*, is not known in a free state. It is probably formed when the oxide dissolves in water,

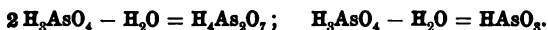


A number of salts (the *arsenites*) are known, which are evidently related to a tribasic acid of this composition. There are certain other salts which may be regarded as derived from a meta-arsenious acid (HAsO_2). All the soluble salts of arsenious acid are exceedingly poisonous. The best antidote in cases of arsenical poisoning is a mixture of freshly precipitated iron hydroxide and magnesia.

200. **Arsenic pentoxide or arsenic oxide** (As_2O_5) is prepared by heating the trioxide to dull redness. It forms a white amorphous mass, which dissolves readily in water, forming arsenic acid (H_3AsO_4), —



of which it may be regarded as the anhydride. Arsenic acid is also obtained by oxidizing arsenious oxide with nitric acid, aqua regia, or other oxidizing agents. The corresponding salts of the metals are called *arseniates*. Arsenic oxide and some of the arseniates are used in the preparation of certain dyes. From this acid, as from the corresponding phosphoric acid, are derived a meta-arsenic acid (HAsO_3) and a pyro-arsenic acid by simply heating the acid, and thus removing water from it:—



At a red heat the meta-arsenic acid loses all its water, and becomes As_2O_5 .

201. **Sulphides of Arsenic.** — Two sulphides of arsenic occur native. One (As_2S_2) is called *realgar*. It is an orange-red body, and may be prepared artificially by heating arsenic and sulphur together in the proper proportions. It is used in pyrotechny. The other (As_2S_3) is called *orpiment*. It is also prepared artificially, and is formed when hydrogen sulphide is passed into an aqueous solution of arsenious oxide, or of an arsenite acidulated with hydrochloric acid in which the sulphide is insoluble. It is used somewhat as a pigment.

Exp. 90. — Into a small bottle put several teaspoonfuls of a hydrochloric acid solution of arsenious oxide, add water enough to nearly fill the bottle, and allow hydrogen sulphide to bubble through the

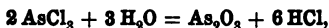
liquid until the liquid smells strongly of it. Collect the precipitate upon a filter, wash it with water on the filter, and test the solubility of the arsenious sulphide in hydrochloric acid and in sodium hydroxide solution.

Arsenic pentasulphide (As_2S_5) separates in the form of a bright yellow powder from the solution of sodium sulpharseniate (Na_3AsS_4) upon the addition of acids.

202. Arsenic Sulphur Salts.—The sulphides of arsenic dissolve in solutions of alkali sulphides with formation of double salts, of which sodium sulpharsenite (Na_3AsS_3) and sodium sulpharseniate (Na_3AsS_4) are examples. These compounds are decomposed by acids, with separation of the corresponding sulphides of arsenic.

203. Halogen Compounds.—The halides of arsenic are analogous to the corresponding compounds of phosphorus, but, unlike phosphorus, arsenic forms only compounds in which the arsenic atom is trivalent, excepting the compounds with iodine, where we have both a tri-iodide (AsI_3) and a penta-iodide (AsI_5).

The reaction of the trichloride of arsenic with water is somewhat remarkable. Treated with much water, it is transformed into the oxide and hydrochloric acid,



while in a small amount of water it dissolves unchanged.

ANTIMONY (Sb).—ATOMIC WEIGHT, 119.

204. Antimony, like arsenic, is found native; it occurs chiefly, however, in the form of a sulphide (Sb_2S_3), which is widely distributed in nature combined with sulphides of copper, lead, nickel, and silver. All the antimony of commerce is obtained from the sulphide. One method of procedure is to heat the mineral with scraps of iron, whereby ferrous sulphide is formed, and antimony set free. The symbol for antimony is **Sb**, from the Latin name of the substance, *stibium*.

205. Antimony is a hard and brittle metal, having a bluish white color, a brilliant luster, and a highly crystalline structure. The cakes of the commercial metal usually present upon their upper surfaces beautiful stellate or fernlike markings. Antimony melts at 450° , gives off vapors at a low red heat, and takes fire at full redness, burning brilliantly with evolution of white fumes of the trioxide (Sb_2O_3). For a metal, it is a poor conductor of heat and electricity.

The metal dissolves in hot, concentrated sulphuric acid, with formation of antimony sulphate, $\text{Sb}_2(\text{SO}_4)_3$, and — unlike phosphorus and arsenic — it can replace the atoms of hydrogen in some other oxygen acids. But in spite of these reactions, the power of antimony to form acids with oxygen, corresponding to those formed by phosphorus and arsenic, shows how closely related it is to these two elements.

Antimony enters into the composition of several very valuable alloys. Type metal is an alloy of lead and antimony, containing about 20 per cent of antimony. For stereotype plates, $\frac{1}{80}$ to $\frac{1}{10}$ of tin is usually added to this alloy. The common white metallic alloys, such as Britannia metal, pewter, etc., used for cheap teapots, spoons, forks, and like utensils, are variously compounded of brass, tin, lead, bismuth, and antimony. The utility of antimony in these alloys depends upon the hardness which it communicates to the compounds, without rendering them inconveniently brittle.

206. **Hydrogen antimonide** (SbH_3), or *stibine*, closely resembles arsine. When a solution of an antimony compound is added to a mixture of zinc and dilute acid from which hydrogen is being disengaged, the antimony compound is decomposed, and a portion of the antimony combines with hydrogen to form *stibine*, which probably has the same atomic and volumetric composition as phosphine and arsine. *Stibine* is a colorless, inodorous gas which resembles hydrogen arsenide in being decomposed by heat; it burns in the air with a whitish flame, and gives off a smoke of antimony trioxide. When a bit of cold porcelain is held against a burning jet of the gas, a sooty spot of metallic antimony is deposited on the porcelain. These spots of metallic antimony are distinguished from those of arsenic, obtained in a similar manner from hydrogen arsenide, by difference in luster, volatility, and solubility in various chemical agents.

Exp. 91 is to be performed precisely like Exp. 86, § 196, except that a solution of an antimony compound is to be substituted for the solution containing arsenic. Reserve the mirrors as in Exp. 86. The same precautions should be observed in the preparation of hydrogen antimonide as in the case of the arsenic compound; for, like it, it is exceedingly poisonous.

Compare the spots obtained on porcelain from arseniuretted hydrogen (Exp. 86) with those obtained from the antimoniuretted hydrogen.

1. The arsenical spot has a metallic luster and a brown color when thin; the stain of antimony has a feeble luster, and is smoky black.

2. The arsenical stain disappears readily on the application of a heat below redness; the stain of antimony is volatile only at a red heat. On account of the comparative want of volatility which characterizes the antimony deposit, the mirrors of antimony obtained in the glass tube are always deposited nearer the heated portion of the tube than the arsenic mirrors are. 3. The arsenical stains may be distinguished, moreover, from the antimonial stains by means of a solution of sodium hypochlorite, which immediately dissolves arsenical spots, but leaves antimonial spots unaffected for a long time. 4. An antimony stain will dissolve readily in a few drops of a solution of ammonium sulphide which has become yellow by keeping (when such a solution is evaporated to dryness, a bright orange stain remains); the arsenical stain, on the contrary, is not perceptibly affected by the yellow sulphide of ammonium, unless heat is applied.

Exp. 92. — Connect the tube of hard glass in which the arsenic mirrors were formed, in Exp. 86, with a hydrogen sulphide generator, interposing between the tube and the generator a suitable drying tube or bottle filled with calcium chloride; then transmit through the tube a *very slow* stream of hydrogen sulphide gas, and heat the mirrors with a small gas flame, proceeding from the outer to the inner border of the mirrors in the direction opposite to that of the gas current. Repeat the same process with the tube containing the antimony mirrors.

207. Antimony and Oxygen. — Antimony forms two well-defined oxides, — *antimony trioxide* (Sb_2O_3) and *antimony pentoxide* or *antimonic anhydride* (Sb_2O_5). Antimony trioxide occurs as a native mineral, and is formed when metallic antimony is burned in the air. A third oxide of antimony occurs native. Its formula is Sb_2O_4 , and it may be regarded as a compound of the other two oxides.



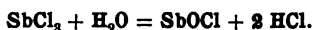
Antimony trioxide (Sb_2O_3) is analogous to arsenious oxide and phosphorous oxide, but differs from them in that it is capable of reacting with strong acids to form salts of antimony: it thus plays a basic part. When it is dissolved in sodium hydroxide, however, there is formed a salt, sodium antimonite (NaSbO_2), which is evidently derived from an acid (HSbO_2), known as *antimonious acid*, which has been isolated, and of which several other salts are known. The trioxide is thus seen to possess both acidic and basic properties.

Antimony Pentoxide (Sb_2O_5). — When antimony is treated with concentrated nitric acid, antimonic acid (H_3SbO_4) is obtained, which, on being gently heated, decomposes into water and the pentoxide Sb_2O_5 , which is thus seen to be the anhydride of antimonic acid. This

oxide readily yields salts of antimonious acid when treated with solutions of bases; but, unlike the trioxide, it is incapable of acting as a basic oxide. As is the case with arsenic acid and phosphoric acid, there can be obtained from antimonious acid a meta-acid (HSbO_3) and a pyro-acid ($\text{H}_4\text{Sb}_2\text{O}_7$), many salts of which are known.

208. Antimony and Chlorine.—Powdered antimony takes fire when thrown into chlorine gas (Exp. 46, § 96); it also combines very energetically with fluorine, bromine, and iodine. When very finely powdered, it is dissolved by boiling hydrochloric acid, with evolution of hydrogen. If a little nitric acid be added to the hydrochloric, the metal dissolves easily, to form a solution of *antimony trichloride* (SbCl_3).

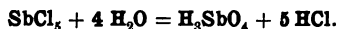
Antimony trichloride, at the ordinary temperature, is a translucent yellowish substance of fatty consistency, whence its popular name, *butter of antimony*. When thrown into water, it is decomposed into hydrochloric acid and antimony trioxide, which, however, remains united with a portion of the chloride, forming a white powder which contains antimony, chlorine, and oxygen, but is somewhat variable in composition. If treated with cold water, only antimony oxychloride is formed,—



Exp. 93.—In a flask of about 200 cc. capacity heat gently 0.5 g. of finely powdered antimony with 30 cc. of strong hydrochloric acid to which 10 drops of nitric acid have been added. When complete solution has been effected, pour a little of the chloride into water, to demonstrate the decomposition just referred to. Evaporate the rest of the solution to the consistency of a thick sirup: it is the *butter of antimony*.

The oxychloride or basic chloride is used as a “mordant” to fix certain organic dyestuffs.

Antimony pentachloride results from the action of an excess of chlorine on antimony or on the trichloride: it is in general much like phosphorus pentachloride. Water converts it into antimonious and hydrochloric acids,—



209. Antimony and Sulphur.—*Antimony trisulphide*, as it occurs in nature, is a black substance with a metallic luster. When prepared by precipitating a solution of antimony tri-



Fig. 41.

chloride by means of hydrogen sulphide, it is an amorphous powder, orange-red in color, which, unlike the trisulphide of arsenic, is readily soluble in concentrated hydrochloric acid. By other processes the trisulphide can be precipitated of almost any color between a light orange and a blackish brown. A vermilion-red sulphide, *antimony vermilion*, has been used as a pigment. Like arsenious sulphide, antimony trisulphide dissolves in solutions of alkali sulphides, forming *sulphantimonites*, such as Na_3SbS_3 (sodium sulphantimonite).

Exp. 94. — Pour some of the antimony trichloride obtained in Exp. 93, § 208, into a small bottle nearly full of water, and then add just enough hydrochloric acid to dissolve the white precipitate which is formed. Through the clear solution pass a stream of hydrogen sulphide. Filter, wash with water on the filter, and test the solubility of the sulphide in dilute hydrochloric acid, in hot strong hydrochloric acid, and in a solution of sodium sulphide.

Antimony pentasulphide is formed by passing hydrogen sulphide through acid solutions of antimonates or of antimonic acid. It is golden yellow when dry, and is known as *golden sulphur* or *golden sulphide of antimony*. The pentasulphide dissolves readily in solutions of alkaline sulphides, forming *sulphantimonates*, of which sodium sulphantimonate (Na_3SbS_4) is an example. Like the corresponding arsenic compounds, the antimony sulphur salts are decomposed by acids, with separation of the corresponding antimony sulphides.

BISMUTH (Bi). — ATOMIC WEIGHT, 206.5.

210. The element **bismuth** is found chiefly in the free state, but occurs also in combination with sulphur, oxygen, and tellurium. It is prepared for the arts almost exclusively from native bismuth. It is a tolerably hard, brittle substance, of a grayish white color, with a reddish tinge and marked metallic luster. When pure, it crystallizes more readily than any of the common metals. By the method of fusion (§ 130) it may be obtained in most beautiful crystals, made highly iridescent by the thin film of oxide which forms on their surfaces while they are still hot.

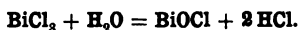
Bismuth promotes the fusibility of metals, with which it is

alloyed to an extraordinary extent. The most remarkable alloy of bismuth is that known as *fusible metal*. When composed of 1 part of lead, 1 part of tin, and 2 parts of bismuth, this alloy melts at 93.75°. At a high temperature, bismuth may be distilled.

211. No compound of bismuth and hydrogen is known as yet. There are three oxides corresponding to the oxides of antimony,— *bismuth trioxide* (Bi_2O_3), *bismuth pentoxide* or *bismuthic anhydride* (Bi_2O_5), and the oxide Bi_2O_4 , which may be regarded as a compound of the other two. Bismuth trioxide exhibits basic characteristics; it reacts with acids to form salts, and is incapable of forming an acid. The pentoxide is *feebly* acidic in character, yielding acids from which a few unstable salts are derived, known as *bismuthates*. The basic character of the trioxide and the feebly acidic character of the pentoxide are in marked contrast with the properties of the corresponding oxides of the other elements of the group. *Bismuth trichloride* (BiCl_3) resembles antimony trichloride. It is decomposed by water into hydrochloric acid, which dissolves a portion of the chloride, and a precipitate containing bismuth, chlorine, and oxygen, and called *bismuth oxychloride* or *basic chloride* (BiOCl). Most of the salts of bismuth are decomposed by water, corresponding basic compounds being formed. The best known of these basic bismuth salts are the basic nitrates and basic carbonates, which are valued medicaments.

212. *Bismuth sulphide* (Bi_2S_3) is formed when hydrogen sulphide is passed through solutions of compounds of bismuth. Unlike the sulphides of antimony and arsenic, it is not soluble in solutions of the alkaline sulphides, and it does not form with them double salts.

Exp. 95.—Heat gently 0.5 g. of finely powdered bismuth with strong hydrochloric acid in a small flask, taking care to avoid any unnecessary excess of the acid. When the metal has dissolved, pour a few drops of the acid solution into a bottle or beaker full of water, and observe the precipitate of white basic chloride which forms, —



To the remainder of the solution add water until a slight cloudiness appears; add then a few drops of concentrated hydrochloric acid to clear the solution, and pass a slow current of hydrogen sulphide through it. Filter out the brownish black precipitate of bismuth sulphide, and, after washing with water on the filter, test its solubility in sodium sulphide solution.

213. **The Nitrogen Group of Elements.**—The five elements, nitrogen, phosphorus, arsenic, antimony, and bismuth, form a

well-marked natural group of elements. In the first place, the elements themselves exhibit a definite gradation of properties; and, secondly, the analogy in composition and properties manifested by the similar compounds of the five elements is most striking and complete.

Nitrogen is a gas; phosphorus, a solid whose specific gravity varies from 1.8 to 2.2; arsenic has the specific gravity of 5.6; antimony, of 6.7; while that of bismuth rises to 9.8. The metallic character is most decided in bismuth, is somewhat less marked in antimony, is doubtful in arsenic, and almost vanishes in phosphorus. The series of corresponding hydrides, oxides, chlorides, and sulphides, which the elements of this group form, are very perfect: they prove the general chemical likeness of the five elements.

| Hydrides. | Oxides. | Oxides. | Oxides. | Chlorides. | Sulphides. |
|------------------------|------------------------------------|------------------------------------|------------------------------------|-------------------------|------------------------------------|
| NH₃ | N₂O₅ | N₂O₄ | N₂O₅ | NCl₃ | P₂S₃ |
| PH₃ | P₂O₃ | Sb₂O₄ | P₂O₅ | PCl₃ | As₂S₃ |
| AsH₃ | As₂O₃ | Bi₂O₄ | As₂O₅ | AsCl₃ | Sb₂S₃ |
| SbH₃ | Sb₂O₃ | | Sb₂O₅ | SbCl₃ | Bi₂S₃ |
| | Bi₂O₃ | | Bi₂O₅ | BiCl₃ | |
| | | | | | P₂S₅ |
| | | | | PCl₅ | As₂S₅ |
| | | | | SbCl₅ | Sb₂S₅ |

When the qualities of the corresponding compounds which the members of the nitrogen group form with other elements are duly taken into account, it will be apparent that the relative chemical power of each element of the group may be inferred from its position in the series of elements:—

$$\text{N} = 14, \text{P} = 30.8, \text{As} = 74.4, \text{Sb} = 119, \text{Bi} = 206.5.$$

The chemical energy of these five elements, broadly considered, follows the opposite order of their atomic weights.

214. The rare elements, vanadium (V), tantalum (Ta), and columbium (Cb), resemble arsenic closely in many properties, and are properly members of the same natural group. Vanadium, although not an abundant element, forms compounds which are used as oxidizing agents in certain processes of dyeing and calico printing.

CHAPTER XV.

SILICON AND BORON.

SILICON (Si).—ATOMIC WEIGHT, 28.2.

215. After oxygen, **silicon** is the most abundant and widely diffused of all the chemical elements. It occurs in combination with oxygen as *silica*, and in combination with oxygen and various metallic elements as *silicates* of those elements.

216. **Silicon dioxide, silicic anhydride, or silica (SiO_2)**, occurs in nature as quartz, flint, rock crystal, agate, etc. It is very hard, and readily scratches glass. It occurs also in plants, particularly in the outer covering of the stalks and the husks of grain. The cuticle of rattan, for example, contains a large proportion of silica; and the same remark is true of most of the grasses and grains. The value of the plant called horsetail (*Equisetum*) as a polishing or scouring agent depends upon the large quantity of silica contained in it. At high temperatures, silica unites readily with oxides of alkali metals and certain other metals to form slags and glasses, many of which are of great importance in the arts. When heated with salts, such as carbonates and sulphates, it decomposes them by virtue of the fact that it is less volatile than some of their constituents: hence it is often spoken of as *silicic acid* by metallurgists and others. At extremely high temperatures, silica is itself somewhat volatile.

217. As it occurs in nature, silica is insoluble in water, but dissolves with more or less difficulty in boiling solutions of the alkali hydroxides, forming sodium (or potassium) silicate. The potassium and sodium silicates are used in the arts under the name of *water glass* or *soluble glass*.

Exp. 96.—To a concentrated solution of water glass contained in a small evaporating dish, add enough strong hydrochloric acid to make the solution acid. There will separate a thick jellylike mass of silicic

acid (H_4SiO_4). Evaporate the contents of the dish to dryness on a water bath, and then heat the residue gently over the gas lamp. The mass will contract in bulk, and, on adding water, there will remain undissolved a fine white powder of silicic anhydride, —



Exp. 97. — Take a very dilute solution of water glass, and add dilute hydrochloric acid drop by drop, until the liquid has a decidedly acid reaction. No precipitation will occur: the silicic acid which is set free, as in the preceding experiment, remains dissolved in the acid liquid. It is possible to remove the chlorides from this solution, and to prepare a pure aqueous solution of silicic acid; but if either of these solutions be evaporated to dryness, and the residues heated, insoluble silicic anhydride will be formed.

218. Silicates. — Silicic anhydride combines with many of the metallic oxides to form *silicates*. Hundreds of silicates occur in nature as crystallized minerals. Thus ordinary feldspar is a double silicate of aluminum and potassium; common mica is a complex silicate of aluminum, iron, and potassium.

219. Glass. — Beside the silicates which occur in nature, there are artificial silicates of great importance in the arts and in everyday life. Sodium silicate (water glass), which has already been alluded to, is extensively used by calico printers and soap makers. It is used to form artificial stone; for, on reacting with calcium hydroxide or carbonate, it forms an insoluble calcium silicate, which may be used to cement together large amounts of sand, or the like. Its chief use, however, is as a component of common glass. The various glasses of commerce are mixtures of a highly siliceous silicate of sodium, or of potassium, or of both these substances, with silicates of other metals, such as calcium, aluminum, and lead. The silicates of the alkali metals are noncrystalline, and, when not too highly siliceous, they are soluble in water; while the silicates of most of the other metals are insoluble, and have a tendency to assume the crystalline form. It has been found that, by combining the alkaline silicates with the silicates of certain other metals, such as calcium, there may be obtained compound glasses, which, while they retain the amorphous character of the alkaline silicates, are capable of resisting the action, not only of air and water, but even of acids and alka-

lies, to a very great extent. Thus, ordinary window glass is composed of silicates of sodium and calcium; Bohemian glass, suitable for ignition tubes, consists of silicates of potassium and calcium, and melts only at a very high temperature; flint glass contains silicates of potassium and lead; bottle glass is a mixture of silicates of calcium, aluminum, iron, and sodium. The silicates of some of the metals are colored. The green color of bottle glass is due to the presence of ferrous silicate; cobalt silicate gives a beautiful blue, manganese silicate a violet, and uranium silicate a yellow, color to the glass.

220. Silica and the silicates are readily attacked by hydrofluoric acid, as has been already seen (Exp. 43, § 91). When silica is treated with dry hydrofluoric acid gas, there is formed a gaseous compound known as *silicon fluoride* (SiF_4), which, in contact with water, decomposes into gelatinous silicic acid, and another compound known as *fluosilicic acid* ($2 \text{HF} \cdot \text{SiF}_4$):—



Exp. 98.—Into a perfectly dry tube of hard glass (No. 5), closed at one end, drop a small quantity (as much as can be taken on the point of a penknife) of a mixture of equal parts of fine quartz sand and powdered fluor spar (calcium fluoride). Moisten the mass with a drop of strong sulphuric acid, and heat it in the flame of the lamp. Gaseous silicon fluoride will escape from the tube; and if a drop of water in the loop of a bit of platinum wire, or on a colored glass rod, be held at the mouth of the tube, the water will be seen to become gelatinous from the formation of silicic acid.

221. Silicon (Si) may be obtained pure from a compound known as potassium fluosilicate. Three allotropic conditions of silicon are known: notably an amorphous variety, which is a brown powder, burning readily in air or oxygen, and forming silicon dioxide (SiO_2); and a variety known as *graphitoid silicon*, crystallizing in lustrous hexagonal plates of a lead-gray color, which resembles graphite (§ 232), and is an excellent conductor of electricity. By exposing the graphitoid



Fig. 42.

form to a high temperature, it is transformed to a diamond-like modification, which occurs in regular octahedral crystals exhibiting a decided metallic luster. Silicon forms with carbon a silicon carbide (SiC), which can be obtained in the form of bluish green crystals. An impure silicon carbide, known as *carborundum*, prepared by the action of a powerful electric current upon a mixture of silica, coke, and salt, is characterized by great hardness and infusibility, and may be used as a substitute for emery.

BORON (B).—ATOMIC WEIGHT, 11.

222. Boron is found in nature in combination with oxygen as *boric* or *boracic acid*, and in combination with oxygen and some metallic element; the most important compound being *sodium diborate*, commonly called *borax*.

In certain volcanic districts in Tuscany, jets of steam mixed with other vapors escape continually from cracks in the soil, and bring to the surface small quantities of boric acid. Since boric acid is not volatile, in the ordinary sense of the term, at temperatures as low as 100° , it appears that it is transported mechanically by the steam, much in the same way that dust is carried along by a current of air. The jets of vapor, laden with acid, are made to bubble through water, as they escape from the earth; and the solution thus obtained is evaporated in pans, beneath which hot currents of vapor from the earth are caused to circulate, until it is concentrated to such a point, that, on cooling, the boric acid crystallizes out.

223. Boron (B).—Of boron itself little need be said. It resembles carbon, in that it may be obtained as a brown amorphous powder by heating its oxide with potassium. It has been obtained also crystallized like the diamond. Hence it appears that there are two allotropic modifications of boron.

224. Boric or boracic acid (H_3BO_3) is but a feeble acid at ordinary temperatures. It may be set free by treating any borate with almost any acid, excepting carbonic acid; though at high temperatures the boric anhydride may expel carbonic acid from its salts, and even decompose sulphates.

Exp. 99.—Dissolve 4 g. of powdered borax, i.e., sodium diborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), in 10 cc. of boiling water, in a beaker or porcelain capsule of 30 or 40 cc. capacity, and add to the solution 2.5 cc. of con-

centrated hydrochloric acid. As the solution cools, boric acid will be deposited in the form of glistening, colorless plates or scales.

225. Boric acid imparts to the flame of burning alcohol a peculiar green tint, which is quite characteristic, and affords a valuable test by which the presence of the acid may be detected.

Exp. 100. — Dissolve a little crystallized boric acid in a teaspoonful of alcohol in a small porcelain capsule. Set fire to the alcohol, and stir the burning solution with a rod, or agitate it by jarring the dish. The flame of the alcohol will be of a fine green color.

226. Boric anhydride (B_2O_3) may be prepared by heating crystallized boric acid, as follows: —

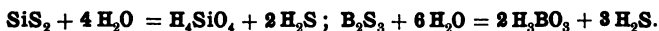
Exp. 101. — In a clean iron spoon heat some crystallized boric acid. The crystals will melt, and, if the heat be continued, the mass will become pasty, and will swell up as the water is expelled. After all the water has been driven off by strong heat, the anhydride is left as a clear, viscous liquid, from which long threads may be drawn out by touching to the surface of the liquid the end of a stick or glass rod, and then gently pulling away the stick with the matter which has adhered to it.

If the fused mass be allowed to cool, it will solidify to a hard, transparent glass, which soon cracks in every direction, and splits up into fragments.

227. Boric acid, when heated, is transformed by loss of water, first into metaboric acid (HBO_2), and then into pyroboric or diboric acid ($H_2B_2O_7$), which gives finally the anhydride B_2O_3 , or boron trioxide. No salts of the normal boric acid (H_3BO_3) are known; those of metaboric acid are rare, and exceedingly unstable. The ordinary borates are all related to diboric acid ($H_2B_2O_7$).

228. Boron, like silicon, forms a gaseous hydride (BH_3); and with chlorine and fluorine also it forms compounds. It is one of the few elements which are capable of combining directly with nitrogen: at a high temperature direct combination takes place, and boron nitride (BN) is formed.

There is a sulphide of silicon (SiS_2) and a sulphide of boron (B_2S_3) analogous to the respective anhydrides. Both these sulphides are decomposed by water, with evolution of hydrogen sulphide, —



These sulphides are white crystalline solids, and are obtained by passing the vapor of carbon disulphide over a mixture of carbon and silicic — or boric — anhydride, strongly heated in a porcelain tube.

CHAPTER XVI.

CARBON (C).—ATOMIC WEIGHT, 12.

229. **Carbon** is an extremely important and a very abundant element. All organic substances, i.e., all things which have or have had life, contain it. It forms part and parcel of all kinds of peat and humus, as well as of the various forms of coal, graphite, petroleum, asphaltum, and all the different varieties of limestone, chalk, marble, and coral. It is found also in the atmosphere and in the waters of the globe; and, though existing therein in comparatively small proportion, it is an ingredient not less essential than either of their other constituents for the maintenance of the actual balance of organic nature. All vegetable and animal life is dependent upon *carbon dioxide*, which exists as a gas in the atmosphere.

230. Three distinct allotropic modifications of carbon are distinguished: namely, (1) the *diamond*; (2) *plumbago* or *graphite*; and (3) ordinary *charcoal* or *lampblack*. Of this last modification there are many subvarieties. In each of its modifications, carbon is an infusible, nonvolatile solid, devoid of taste and smell. While the several modifications differ among themselves in color, hardness, luster, specific gravity, behavior towards chemical agents, power of conducting heat and electricity, and in various other respects, they all agree in this: that, on being strongly heated in presence of oxygen, they unite with it and form the same compound, an oxide of carbon (CO_2).

231. **Diamond.**—The diamond is pure, or nearly pure, carbon, and occurs in nature in octahedral crystals. Its rarity and its high refractive power as regards light, together with the difficulty with which it is worked, make it the most precious of gems. It is the hardest known substance. Small diamonds have been found in certain meteorites; and minute specimens

have been prepared artificially by cooling melted cast iron under high pressure, when some of the carbon of the cast iron passes into the diamond form.

The diamond is not attacked by the strongest acids or alkalis, not even by hydrofluoric acid; nor is it acted upon by any of the nonmetallic elements, with the exception of oxygen at high temperatures. At the ordinary temperature of the air, diamond undergoes no appreciable change. Out of contact with the air, or in an atmosphere which has no chemical action upon it, it suffers no alteration at the highest furnace heat; heated white-hot between the charcoal poles of a powerful galvanic battery in a vacuum, it softens and swells up, forming a black, brittle mass like coke; heated in oxygen gas, it burns to carbon dioxide (CO_2).

232. **Graphite**, or **plumbago**, sometimes called **black lead**, is familiarly known as the material of common lead pencils. It is found as a mineral in nature in various localities. It occurs both in the form of crystals and in the amorphous, massive state. In both forms it is always opaque, of a black or lead-gray color and metallic luster.

Graphite is very friable. When rubbed upon paper, it leaves a black, shining mark, whence its use for pencils. Amorphous graphite is so soft and unctuous to the touch, that it is often used as a lubricant for diminishing the friction of machinery; but, in spite of this seeming softness, the particles of which the masses of graphite are composed are extremely hard. They rapidly wear out the saws employed to cut these masses. In the air, at ordinary temperatures, graphite undergoes no change; hence its use for covering iron articles to prevent their rusting. By virtue of its greasy, adhesive quality, it is easy to cover iron with a thin, lustrous layer or varnish of it: the common stove polishes, for example, are composed of powdered graphite. Graphite is a good conductor of electricity, and is on this account much used for coating surfaces of wood, plaster, and wax, and other nonconducting materials, so as to render them capable of conducting the electric current, and so receiving a metallic film in the processes of electroplating. Even at very high temperatures it is scarcely at all acted on by

the oxygen of the air. It is, moreover, altogether infusible; hence it is usefully applied in the manufacture of highly refractory crucibles, known as *black-lead* or *plumbago crucibles*.

233. Gas Carbon. — An interesting subvariety of carbon somewhat similar to graphite, and standing, as it were, between it and the ordinary modification of carbon, is obtained from the retorts in which common illuminating gas is manufactured. It is known as *gas carbon*, or *carbon of the gas retorts*, and results from the burning-on of drops of tar upon the interior walls of the retort, and the long-continued heating of the crust thus formed.

Gas carbon is very hard, compact, and dense. It has a metallic luster, and conducts electricity like a metal. On account of its high conducting power, it is employed in the manufacture of galvanic batteries, and of pencils for the electric lamp.

234. Coke and anthracite coal are impure subvarieties of carbon, which, from the chemical point of view, may be classed either with graphite or charcoal, or, better, between the two. They are less like graphite, however, than gas carbon is. Coke is the residue resulting from the destructive distillation of soft or bituminous coal.

Exp. 102. — Put into a tube of hard glass (No. 1), 12 or 15 cm. in length, enough bituminous coal, in coarse powder, to fill one third of the tube. Fit to this ignition tube

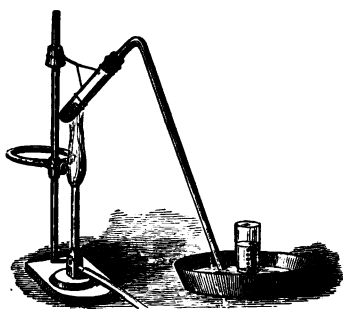


Fig. 43.

a large delivery tube of glass (No. 4), and support the apparatus upon the iron stand, as shown in the figure. Heat the coal in the ignition tube, and collect in bottles the gas which will be evolved. The gas will burn with a yellow flame on the application of a match. This gas is, in the main, a mixture of several compounds of carbon and hydrogen. It is, in fact, ordinary illuminating gas.

As soon as gas ceases to be given off from the coal, take the end of the delivery tube out of the water, and, when the ignition tube has become cold, break it, and examine

the coke which it contains. Much of the coke used for domestic purposes is obtained as an incidental product in the manufacture of illuminating gas.

Bituminous coal is a substance of vegetable origin, which appears to have been formed from plants by a process of slow decay going on without access of air, and under the influence of heat, moisture, and great pressure. Like vegetable matter in general, it is composed of carbon and hydrogen, together with small proportions of oxygen and nitrogen, and a certain quantity of earthy and saline substances, commonly spoken of as inorganic matter. On being heated in the air, it burns away almost completely after a while, leaving nothing but the inorganic components as ashes. But when heated out of contact with the air, — that is to say, when subjected to *destructive distillation*, as in Exp. 102, — the volatile hydrogen is all driven off in combination with some carbon, either as gas or as a tarry liquid; and the residue, or coke, contains only carbon contaminated with the inorganic matters originally present in the coal. Large quantities of coke are made for metallurgical uses, especially in countries which have no mines of anthracite. The gas resulting from the decomposition of the coal is in this case commonly allowed to go to waste; and the operations are so conducted, that firm, hard, compact coke shall be obtained. When substances are subjected to destructive distillation, the bodies obtained do not exist as such before the distillation, but are formed by a rearrangement of the atoms under the influence of heat.

Anthracite is supposed to have been formed, like bituminous coal, from the slow decay of vegetable matter, and then to have been subjected to some sort of natural distillation, by which it has been deprived of nearly all the hydrogen, nitrogen, and oxygen of the original wood. It is thus, in some sort, a very hard coke, formed by natural agencies.

235. Both coke and anthracite are hard and lustrous. As compared with charcoal, they are rather difficult of combustion. Both anthracite and coke — the latter in spite of its porosity — conduct heat readily, as compared with charcoal; hence one reason of the difficulty of kindling them. In building a charcoal fire, the heat evolved by the combustion of the kindling material is almost all retained by the portions of charcoal immediately in contact with the kindling agent; but in the case of coke or anthracite, a large proportion of this heat is conducted off, and diffused throughout the heap of fuel, so that no portion of the fuel can at once become very hot.

236. Charcoal, or lampblack, is commonly taken as the representative of the third or amorphous modification of carbon. To obtain this variety of carbon in a state of tolerable purity, sugar, starch, or some other substance which contains no mineral constituents, may be heated in a closed vessel out of contact with air; or petroleum, oil of turpentine, or natural gas may be burned in a quantity of air insufficient for their complete combustion.

Charcoal can be obtained by distilling wood in retorts in the same way that we have seen that coke can be procured from bituminous coal (Exp. 102, § 234).

Exp. 103.—Provide an ignition tube and a delivery tube similar to those employed in Exp. 102, § 234. Fill the ignition tube with shavings or small fragments of wood, arrange the apparatus as before, and light the gas lamp. Collect in bottles the gas which is given off from the wood, and test it as to its inflammability by applying a lighted match. After the flow of gas has ceased, remove the end of the delivery tube from the water, plug it so that no air can enter the ignition tube, and lay the apparatus aside until it has become cold. Finally remove the cork from the ignition tube, and take out the charcoal which is contained in it. Heat a portion of this charcoal upon platinum foil, and observe the manner in which it burns. It will illustrate the fact that solid substances which are incapable of evolving volatile or gaseous matter do not burn with flame: they merely glow.

For use in the arts, charcoal is sometimes prepared by distilling the wood in retorts, but more generally by burning the wood with little access of air. Logs of wood are piled up into a large mound or stack around a central aperture, which subsequently serves as a temporary chimney, and also for the introduction of burning substances for firing the heap. The finished heap is covered with chips, leaves, sods, and a mixture of moistened earth and charcoal dust, a number of apertures being left open around the bottom of the heap for the admission of air and the escape of the products of distillation and combustion. The heap is kindled at the center, and burns during a fortnight. When the process is judged to be complete, all the openings are carefully stopped, in order to extinguish the fire, and the heap is then left to itself until cold. The charcoal retains the form of the wood,—the shape of the knots and the

annual rings of the wood being still perceptible in it, — but it occupies a much smaller volume than the wood. Generally its bulk does not amount to more than three fourths of that of the wood, and its weight never exceeds one fourth the weight of the wood. Sometimes kilns built of brick are used instead of the rude heaps here described.

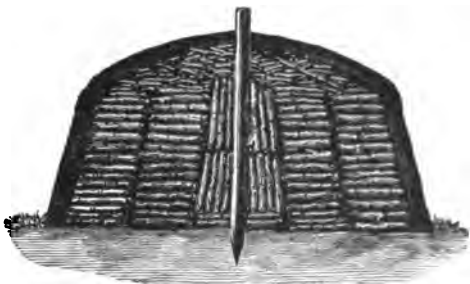


Fig. 44.

Where charcoal is prepared by distilling wood in retorts, the liquid products of distillation, namely, tar, acetic acid (pyroligneous acid), wood spirit, etc., are saved and utilized.

237. Lampblack. — Upon the large scale, lampblack is manufactured by heating organic matters, such as tar, petroleum, resin, or pine knots, which contain volatile ingredients very rich in carbon, until vapors are disengaged, and then burning these vapors in a current of air insufficient for their complete combustion. The vapors consist of compounds of carbon and hydrogen; and, the supply of air being insufficient to consume both hydrogen and carbon, a large portion of the carbon of the combustible does not burn, but is deposited as a very fine powder, precisely similar to that which constitutes the black portion of common smoke. Lampblack may be prepared also by burning natural gas in a limited supply of air. As obtained from this source, it is particularly pure, and is easily compressible; hence it is preferred for making some kinds of printer's ink and for the pencils of electric arc lights. Enormous quantities of lampblack are used for mixing with pigments, for making printer's ink, for coloring fertilizers, etc.

Exp. 104. — Fill an ordinary spirit lamp (Appendix, § 5) with oil of turpentine; light the wick, and place over it an inverted wide-mouthed bottle of the capacity of a liter or more, one edge of the mouth of the bottle being propped up on a small block of wood, so that some air

may enter the bottle. As the supply of air is insufficient for the perfect combustion of the oil of turpentine, a quantity of lampblack will separate, and be deposited upon the sides of the bottle.

Hydrogen kindles at a lower temperature than carbon; hence, if the flame of a burning compound of carbon and hydrogen be cooled down below the temperature at which carbon takes fire, lampblack will be formed, even if there be present an abundant supply of air.

Exp. 105. — Press down upon the flame of an oil lamp or candle an iron spoon or a porcelain plate in such manner that the flame shall be

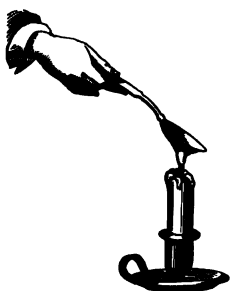


Fig. 45.

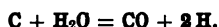
almost, but not quite, extinguished. The solid body not only obstructs the draught of air, and thereby interferes with the act of combustion, but it also cools the flame by actually conducting away part of its heat. The temperature is thus reduced to below the kindling point of carbon, and a quantity of lampblack remains unconsumed and adhering to the spoon or plate. The deposit of lampblack is, of course, comparable with the spots of arsenic and antimony alluded to in §§ 196, 206, as being obtained upon porcelain, as products of the incomplete combustion of the hydrogen compounds of these elements.

238. In all its varieties, charcoal is a very important chemical agent, chiefly because of the readiness and energy with which it combines with oxygen at high temperatures. It might almost be said that the art of metallurgy, as it now exists, is based upon the affinity of carbon for oxygen.

Exp. 106. — Mix 2.5 g. of copper oxide with 0.25 g. of powdered charcoal; place a portion of the mixture in an ignition tube made of No. 3 glass, and heat it strongly in the gas lamp. The charcoal will unite with the oxygen of the copper oxide, and the compound thus formed will escape in the form of gas, while metallic copper will remain in the tube.

This experiment is analogous to Exp. 88, § 198, where arsenious acid was reduced by means of charcoal. Both experiments are typical of the manner in which hot charcoal acts upon metallic oxides. At a white heat, it removes oxygen from its combinations with some elements which hold it with great force, such as the oxides of sodium and potassium, phosphoric acid, and water. If a current of steam be

passed over red-hot charcoal, the steam is decomposed, the hydrogen is set free, and the oxygen of the steam combines with a portion of the carbon to form carbon monoxide (CO), an inflammable gas. The reaction which occurs may be formulated as follows:—



The *deoxidizing* power of charcoal, thus illustrated, is exhibited only at high temperatures. At the ordinary temperature of the air, the chemical energy of charcoal is exceedingly feeble. Charcoal is, in fact, one of the most durable of substances. Specimens of it have been found at Pompeii and upon Egyptian mummies, to all appearance as fresh as if just prepared: the action of the air continued through centuries has exerted no appreciable influence upon it. Fence posts which are sunk for a certain distance into the ground are often charred on the outside, and thus rendered more durable.

239. A physical property of charcoal, which is of great practical importance, is its power of *absorbing* and *condensing* within its pores a great variety of gases and vapors. Freshly burned charcoal exposed to damp air—in a cellar, for instance—will gain 10 or 12 per cent in weight in the course of a single day.

Exp. 107.—Take from the fire a piece of charcoal which has been heated to full redness for some time; thrust it under water, so that it may be suddenly cooled; and observe that it sinks in the water, and that few or no bubbles of gas escape from its pores.

Take another piece of charcoal which has long been exposed to the air and has not recently been heated, attach to it a quantity of sheet lead sufficient to sink it in water, and immerse the whole in a large beaker two thirds full of hot water. The mobile water will immediately enter the pores of the charcoal, and a portion of the air which had previously been absorbed by these pores will be driven out, and can be seen escaping in bubbles through the water, chiefly from the broken ends of the coal.

To the presence of air and aqueous vapor which has been thus absorbed, are to be attributed the snapping and crackling of old charcoal when it is thrown upon a hot fire.

Different gases are absorbed by charcoal in very different proportions: thus a cubic centimeter of dry, compact charcoal, such as that from boxwood, will absorb as much as 90 cc. of ammonia gas in the

course of 24 hours; while in the same time it will absorb only 35 cc. of carbonic acid, and only 2 cc. of hydrogen.

240. Charcoal is much employed as a *disinfecting agent*. It is capable of removing many offensive odors from the air, such, for example, as the fetid products given off during the putrefaction of animal and vegetable substances. Animal matter in an advanced stage of putrefaction loses all offensive odor when covered with a layer of charcoal, and the flesh of a dead animal buried beneath a thin layer of charcoal will gradually waste away and be consumed without exhaling any unpleasant smell.

Exp. 106. — Place a small quantity of powdered charcoal in a bottle containing hydrogen sulphide gas, and shake the bottle. The odor of the hydrogen sulphide will quickly disappear. In the same way an aqueous solution of hydrogen sulphide (Exp. 70, § 136) can be deodorized by filtering it through a layer of charcoal.

In all these cases the use of charcoal as a disinfectant depends not merely upon its mechanical ability to absorb offensive gases, but also, and mainly, upon the fact that the absorbed gases are chemically destroyed within the pores of the coal by the oxygen which has been condensed into these spaces from the air. The purifying action depends upon *oxidation*, upon the burning-up of the offensive gases. The charcoal is not to be regarded as an *antiseptic* or preservative agent proper to prevent decay; on the contrary, it may actually hasten the destruction of putrescible organic matters. Under ordinary circumstances, the pores of charcoal contain more or less oxygen which has been absorbed from the air, and any new gas which is dragged in is forced into intimate contact with this oxygen. If the new gas is one on which oxygen can act, it is destroyed; and, as fresh portions of the gas are absorbed by the charcoal, additional quantities of oxygen are also absorbed, so that the action may go on for a long time. A great merit of charcoal as a disinfectant is, that it constantly draws in to destruction the offensive matters around it. Pans of charcoal placed about a room—the wards of a hospital, for example—the air of which is offensive, act to remove the unpleasant smell.

241. Charcoal not only destroys odors, but it removes colors as well; and for this purpose it has long been employed in the purification of sugar and of many chemical and pharmaceutical preparations. Almost any organic coloring matter can be removed from a solution by filtering the liquid through a layer of charcoal.

Exp. 109. — Provide four bottles of the capacity of 100 or 200 cc., and place in each of them a tablespoonful of boneblack (§ 242). Into the first bottle pour a quantity of the blue compound of iodine and starch obtained in Exp. 59, § 112; into the second, a decoction of cochineal; into the third, a dilute solution of soluble indigo blue; into the fourth, a solution of blue litmus, of logwood, or indeed of almost any other vegetable coloring matter; enough of the solution being taken in each instance to nearly fill the bottle. Cork the bottles and shake them violently, then pour the contents of each upon a filter (Appendix, § 15), and observe that the filtrate is in each instance colorless, or nearly so. In case the first portions of the filtrate happen to come through colored, they may be poured back upon the filter, and allowed to again pass through the coal.



Fig. 46.

In the purification of brown sugar, the coloring matters are removed in a manner similar to the foregoing, the colored sirup being filtered through layers of boneblack. Beside coloring matters, charcoal can absorb many other substances: sulphate of quinine, for example, is removed from its solutions to a very considerable extent by charcoal; and the same remark applies, with perhaps still more force, to strychnine. The bitter principle of the hop, "lupulin," may be entirely removed from ale by filtering the latter through boneblack.

In all these cases where coloring matters, and the like, are removed from solutions, the action of the coal appears to depend in the main directly upon the physical property of *adhesion*; the subsequent oxidizing action being here far less clearly marked than in the instances previously studied (§ 240), where gases are acted upon. Much of the absorbed color or other matter will usually be found attached to the surfaces of the coal, undecomposed and unaltered.

242. As obtained from different sources, charcoal exhibits very different degrees of *decolorizing* power; but of the varieties commonly met with, and to be procured in commerce, those known as *boneblack*, *bone charcoal*, or *bone char* are the most efficient. Bone char is prepared for the use of sugar refiners

by subjecting bones to destructive distillation in large iron cylinders, and carefully cooling the charcoal out of contact with the air. As dry bones contain about 66 per cent of mineral matter, the charcoal thus obtained is left in an exceedingly porous condition, distributed over and among the particles of the mineral matter.

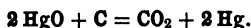
243. Compounds of Carbon and Oxygen.—There are two of these compounds, — *carbonic anhydride* (CO_2) and *carbon monoxide* (CO).

244. Carbon dioxide, or carbonic anhydride (CO_2), commonly called **carbonic acid** in ordinary speech, is always formed when carbon or any of its compounds is burned in an excess of air or of oxygen gas, or in contact with substances, gaseous, liquid, or solid, which are rich in oxygen, and yield it readily to other bodies.

Exp. 110.—Place a live coal (charcoal) upon a deflagrating spoon, and thrust it into a bottle full of air, or, better, oxygen gas. When the coal has ceased to glow, pour into the bottle some limewater, — a solution of common slaked lime in water, — and shake the bottle. The liquid will become milky and turbid, and, when left at rest, will deposit a white powder (calcium carbonate). The presence of carbonic acid can readily be detected by means of limewater, since this insoluble precipitate of calcium carbonate is formed when the two substances are brought together.

From the formulas of the class of bodies known as *carbonates* (sodium carbonate = Na_2CO_3), we should infer the existence of a carbonic acid of the formula H_2CO_3 . Carbonic anhydride does dissolve in water, and the solution has a slightly acid reaction; it is, however, doubtful if a definite compound is formed. The term *carbonic acid*, as applied to the higher oxide of carbon (CO_2), has been so long in familiar use, and has become so completely a part of our language and literature, that it will be used frequently in this chapter in its popular sense.

Exp. 111.—As was just now said, carbonic acid may be produced by heating carbon in contact with solid bodies which contain oxygen; such, for example, as the red oxide of mercury. Mix 11 g. of red oxide of mercury with 0.33 g. of charcoal; place the mixture in an ignition tube arranged as in Fig. 43; heat the tube, and collect over water the gas which is evolved. Test the product with limewater, as in Exp. 110, § 244. The reaction may be written as follows:—



The metallic mercury set free condenses in droplets upon the cold upper portions of the ignition tube.

245. Carbon dioxide may readily be obtained from certain compounds called *carbonates*, several of which are abundant minerals. Common marble and limestone, for example, are composed of calcium carbonate; and carbonic acid can readily be obtained by heating them very strongly, or by subjecting them to the action of acids.

Exp. 112.—In a gas bottle of 500 or 600 cc. capacity, arranged precisely as for generating hydrogen (Exp. 18, § 37), place 10 or 12 g.

of marble in small lumps; cover the marble with water, and pour in through the thistle tube concentrated hydrochloric acid, by small portions, in such quantity as shall insure a continuous and equable evolution of gas. Collect several bottles of the gas over water, then replace the anterior portion of the delivery tube with a straight tube, and collect one or two bottles of the gas by down-



Fig. 47.

ward displacement. Carbonic acid gas is half as heavy again as air. The reaction between the calcium carbonate and the hydrochloric acid may be thus formulated:—



246. At the ordinary atmospheric temperature and pressure, carbon dioxide is a transparent, colorless gas, of a slightly acid smell and taste. It is *incombustible*, being already the product of the complete combustion of carbon, and is, moreover, incapable of supporting the combustion of most other bodies; it is also incapable of supporting animal life.

Exp. 113.—Thrust into a bottle of the gas obtained in Exp. 112, § 245, a lighted candle, or, better, a large flame of alcohol burning upon a tuft of cotton. In either case the flame will be instantly extinguished.

247. The specific gravity of carbonic acid gas is 22. Being thus 1.53 times heavier than air, it can be poured from one vessel to another almost as readily as if it were water.

Exp. 114. — From a large bottle or other vessel full of the gas, pour a quantity of carbon dioxide upon the flame of a lamp or candle; that is to say, hold the mouth of the open bottle of carbon dioxide obliquely over the candle flame, so that the gas shall fall like water upon it: the flame will immediately be extinguished.



Fig. 48.

Owing to the great weight of carbon dioxide, it often accumulates in wells, and other deep cavities in the earth, in places where the continual generation of it by the decomposition of organic substances cannot be overcome by the low diffusive power of the gas (§ 41). Carbon dioxide mixes with air very slowly; but, when once mixed with air, it has no further tendency to settle down or to separate itself in any way.

Exp. 115. — Over a bottle filled with carbon dioxide, invert another bottle full of air, in such a manner that the mouth of the upper inverted bottle shall rest upon that of the upright bottle full of carbon dioxide. After an hour or so, pour limewater into each of the bottles and shake them separately: the limewater will become turbid in each case from the formation of calcium carbonate, for a part of the carbon dioxide will have diffused and ascended out of the lower bottle. The two gases will become completely blended, if time enough be allowed; the heavy carbon dioxide diffusing upwards into the air, and the lighter atmospheric air diffusing downwards into the carbon dioxide.

The great importance of this diffusion of gases, in the economy of nature, is well illustrated by this case. Whenever, as in the processes of respiration, combustion, and decay, oxygen is withdrawn from, and carbon dioxide is thrown into, the air, the carbon dioxide and the nitrogen, with which it is accompanied, immediately mix with the surrounding air, and distribute themselves through the atmosphere. The composition of the atmosphere is thus maintained uniform all over the globe. It is only in confined places, where nearly pure carbon dioxide is produced more rapidly than it can pass off by diffusion, that it accumulates to any appreciable extent.

Carbon dioxide is not, strictly speaking, poisonous. An atmosphere containing 5 per cent of it can be breathed without serious results; but, just as it cannot support ordinary combustion, so it cannot support respiration, because it is unable to supply the oxygen necessary for life. Animals die in it by suffocation.

Carbon dioxide can be obtained in the liquid state by subjecting the gas to pressure. It can also be obtained in a solid, snowlike state by exposing the liquid to cold.

248. Carbon dioxide is soluble in water to a considerable extent. One volume of water, at the ordinary temperature and pressure, will dissolve one volume of the gas, but its solubility increases if the pressure be increased.

Exp. 116. — Into a long-necked flask or phial filled with carbon dioxide, pour a quantity of water; close the bottle with the finger and shake it; immerse the mouth of the bottle in water, and remove the finger: water will rush into the bottle to supply the place of the gas which has been dissolved. Again place the finger upon the mouth of the bottle, shake the bottle as before, and subsequently open it beneath the surface of the water: a fresh portion of water will flow into the bottle to supply the new vacuum. In this way, by repeated agitation with water, all of the carbon dioxide in the bottle can be absorbed.

When subjected to increased pressure, carbonic acid gas dissolves in water much more abundantly than at the ordinary pressure of the air. Water thus surcharged with carbonic acid has an agreeable, acid, pungent taste, and effervesces briskly when the compression is suddenly removed, as when the liquid is allowed to flow out into the air; for the excess of the gas over what is soluble at the normal pressure escapes. Such carbonic acid water flows from the earth in many localities, as at Selters, or Seltz, in Germany (Seltzer water), and at Saratoga, N.Y. It is also prepared artificially in large quantities, and sold as a beverage under the technical name of *soda water*. The effervescent qualities of fermented liquors, such as cider, champagne, and beer, are in like manner dependent upon the presence of compressed carbon dioxide. Water containing carbon dioxide can dissolve many substances which are but slightly soluble in pure water.

249. Carbon dioxide is produced, not only in the actual combustion of all substances which contain carbon, but also during the *decay* and *putrefaction* of all animal and vegetable substances. During *fermentation* it is evolved in large quantities, and it is continually given off during the *respiration* of animals.

Exp. 117. — Dissolve 10 g. of honey or molasses in 100 cc. of water; fill a large test tube with the mixture, and crumble into it a small bit of compressed yeast. Close the open mouth of the test tube with the

thumb, and invert it in a small saucer or porcelain capsule filled with the diluted sirup. Place the saucer and tube, with their contents, in a warm place, having a temperature of about 20° or 30°, and leave them there during 24 hours. In a short time, fermentation sets in, and the sugar of the sirup is gradually converted into alcohol and carbonic acid.



The carbonic acid thus formed rises in minute bubbles, causing a gentle effervescence in the liquid, and collects in the upper part of the tube, while the alcohol remains dissolved in the liquid.

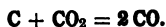
Exp. 118. — Provide two small bottles; place in each 15 or 20 cc. of limewater; through a glass tube, blow into the limewater of one of the bottles air coming from the lungs. By means of bellows, to the nozzle of which a gas delivery tube has been attached, force through the limewater of the second bottle a quantity of fresh air. The clear liquid of the first bottle will quickly become turbid through deposition of calcium carbonate, while the limewater of the second bottle will remain clear for a long while; but, if a sufficient quantity of air be forced through it, the liquid will finally become turbid from the action of the small amount of carbon dioxide present in the air.

250. From the foregoing it appears that in the usual processes called *life*, *fermentation*, *decay*, and *combustion*, there is involved chemical action: in all of these processes oxygen from the air unites with carbon, while carbon dioxide is set free and thrown into the atmosphere. The question naturally arises, What becomes of all this vast amount of carbon dioxide coming into the atmosphere from the respiration of animals, from fires, from decaying and fermenting substances, and from various other sources? If the carbon dioxide remained in the air, the latter would, after a while, become unfit to support animal life. But it has been found that the average proportion of carbon dioxide in the air does not increase; and, on the other hand, it is found that the proportion of oxygen in the air does not undergo any appreciable change, in spite of the enormous volume of it which is absorbed in the processes of breathing, combustion, and decay, above enumerated. For, unlike animals, green-leaved plants take in carbon dioxide and give out oxygen. The leaves of plants are so constructed that they can decompose carbon dioxide in sunlight, and fix carbon for the building-up of the plant, while oxygen is set free. This reciprocal action of plants and animals, tending to maintain unchanged the constitution of the atmosphere, is one of the most wonderful adjustments of nature. Some carbon dioxide is also removed from the atmosphere by solution in rain, and is thus carried into the soil, where, together with that formed by the decay of humus, it may react upon basic substances to form carbonates.

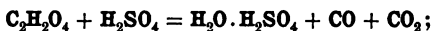
251. It may be assumed that carbonic acid (H_2CO_3) exists in the solution, just now studied, of carbon dioxide in water. In this point of view, the dioxide is the anhydride of the acid. Carbonic acid is a good example of a weak acid: it fails to neutralize (§ 67) completely the alkalinity of strongly basic hydroxides, such as those of sodium and potassium. Both the sodium carbonates, for example, have a decidedly alkaline reaction, and so also has bicarbonate of lime. Almost all carbonates are readily decomposed by acids—even by very weak acids—with an effervescence caused by the escape of carbon dioxide: many among them—such as calcium carbonate, for example—are decomposed by heat.

Carbonic acid is dibasic (§ 70), like sulphuric acid: thus there is a sodium carbonate (Na_2CO_3) and a sodium acid carbonate, the so-called *bicarbonate of sodium* (NaHCO_3).

252. Carbon monoxide (CO), called also carbonic oxide, may be prepared by passing carbon dioxide over hot charcoal,—



This method of formation is illustrated in an ordinary fire of anthracite, coke, or charcoal. The oxygen of the air coming in contact with the hot fuel at the lower part of the fire combines with the carbon to form carbon dioxide, which, as it rises through the heated coal, leaves there a part of its oxygen, and is converted into carbon monoxide, which, as it escapes from the upper portion of the fire, again combines with oxygen, or *burns*, with the familiar blue flame noticed flickering above an anthracite fire. Carbon monoxide is always formed when a substance containing carbon burns in insufficient supply of air. An easy method of obtaining carbon monoxide is to decompose oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$, § 410) by means of strong sulphuric acid. On heating the mixture, the sulphuric acid removes the elements of water from the oxalic acid, which breaks up into carbon dioxide and carbon monoxide,—



or it may be obtained by heating the oxides of almost any of the metals with an excess of charcoal. The gas is, however, contaminated with carbon dioxide in both these methods. It may be prepared pure as in the following experiment.

Exp. 119.—In a flask of about 250 cc. capacity, provided with a delivery tube and with a safety tube (Fig. 49), heat *gently* a mixture

of 5 g. of finely powdered potassium ferrocyanide (yellow prussiate of potash) and 40 or 50 g. of strong sulphuric acid. Collect the gas over water, and test it as to its inflammability. Thrust also a lighted splinter into the gas, and observe that it will be extinguished. The reactions which occur between the chemicals employed will be explained in a subsequent section (§ 472).

253. Carbon monoxide is a transparent, colorless gas, having no odor; it may be liquefied, but with great difficulty. The gas is somewhat lighter than air, its specific gravity being 14, while that of air is 14.5. It is but little soluble in water, and may be collected over water without much loss. It extinguishes combustion just as hydrogen does, and destroys animal life. Unlike hydrogen and nitrogen, however, it is a **true poison**. Apparently it combines with and alters the character of the red corpuscles of the blood. Thus it destroys life, not negatively, by mere suffocation or exclusion of oxygen, but by direct noxious action. It is the presence of this gas which occasions the peculiar sensation of oppression and headache which is experienced in rooms into which the products of combustion have escaped from fires of charcoal or anthracite. Carbon monoxide is the most dangerous of the gases given off from coal fires. Fortunately, as thus set free in rooms, etc., it is usually mingled with other gases having peculiar odors, and thus the presence of coal gas is noticed. An atmosphere containing so small an amount as 0.5 per cent of carbon monoxide may give rise to alarming symptoms. The chief danger also in breathing air which is contaminated with illuminating gas depends on the presence of carbon monoxide. Much of the ill repute which attaches to carbon dioxide really belongs to carbon monoxide; for, since both these gases are produced by burning charcoal, many persons are liable to confound them; but the dioxide is, comparatively speaking, almost innocuous.

254. Carbon monoxide plays a very important part in many metallurgical operations, on account of the power which it possesses, at high temperatures, of taking away oxygen from many compounds containing that element. Much of the reducing action which is, commonly speaking, attributed directly to carbon, is really effected, in practice, through the mediation of the monoxide.

255. Carbon monoxide burns readily in the air, the sole product of the burning being carbonic acid. The monoxide forms an explosive mixture with air or oxygen.

Exp. 120. — To the apparatus employed in Exp. 119, § 252, provided air has not been allowed to enter by the cooling-down of the mixture, attach a piece of glass tubing drawn out at the end (but not to a very fine point) and bent in such manner that a stream of gas may be delivered upwards from the point. Light the gas as it flows out of the tube, and hold over the pale blue flame a clean, dry bottle. No moisture is deposited. That carbon dioxide has been produced may be proved by pouring a little limewater into the bottle and shaking it about in the gas therein contained.



Fig. 49.

256. **Carbonyl Compounds.** — When carbon monoxide acts as a compound radical, it is termed *carbonyl*, and the compounds it forms are known as *carbonyl compounds*.

257. **Combustion.** — Now that we have become acquainted with carbon, hydrogen, and oxygen, and with some of the more important compounds formed by the union of these elements, the subject of combustion can be more fully discussed than has been possible hitherto. The materials employed as combustibles are, as a general rule, compounds of carbon and hydrogen. There are some exceptions to this rule, as when the metal magnesium is burned for light, or the heating of a sulphuretted ore is effected by the combustion of its own sulphur.

258. In almost all cases, artificial light results from the incandescence of particles either of solid matter or of dense vapors. When the heat, which is an invariable accompaniment of chemical combination, can play directly upon such solid or semisolid particles with force enough to ignite them,

an exhibition of light will accompany the chemical change. The hydrogen flame affords no light, or as good as none, because in it nothing but a highly attenuated gas is heated. But when a solid body, such as the platinum wire or the piece of lime of § 43, is placed in this nonluminous hydrogen flame, intense light is radiated from the heated solid.

Exp. 121. — Sprinkle fine iron filings into the flame of an alcohol lamp, or into the nonluminous flame of the gas lamp, and observe the light given off by the particles of metal as they become incandescent while passing through the flame; or rub together two pieces of charcoal above a nonluminous flame, in such manner that charcoal powder shall fall into the flame.

259. In ordinary luminous flames, such as those of candles, lamps, and illuminating gas, the ignited substance is carbon, or rather a vapor or fog of certain carbon compounds containing more or less hydrogen.

Ordinary illuminating gas may be decomposed by passing it through a tube heated red-hot; the carbon will separate, in a finely divided state, while hydrogen will escape from the tube: or, by putting a cold body into a luminous gas flame, the carbon is deposited as soot (Exp. 105, § 237). This breaking-up of the compounds of carbon and hydrogen under the influence of heat takes place when the gas is burned in the air; and, if the supply of air furnished be insufficient to convert all the carbon and hydrogen to carbonic acid and water, the particles of carbon which escape unconsumed will cause the flame to be *smoky*. If the supply of air be excessive, the combustion will be complete, and no light will be afforded by the flame.



Fig. 50.

If we unscrew the tube of a common Bunsen lamp (Appendix, § 5), and light the gas as it issues from the slit (or holes) in the lower part of the burner, we shall have a luminous and perhaps even smoky flame. When, however, the tube is in its place, the gas becomes mixed with air, which enters by the holes at the base of the lamp; and when the mixture is

lighted, the gas is in intimate contact with air enough to burn it at once, and completely. A luminous flame may also be produced by simply closing the holes at the base of the lamp.

If across the top of the chimney of a lighted Argand gas burner, which is burning with a low flame, we slowly slip a strip of sheet iron, and thus obstruct the flow of air, the flame will increase in size, becoming more and more luminous, and finally will actually smoke. The amount of gas supplied has remained the same. The difference in the amount of light is owing to the decrease of the supply of air. The murky flame, such as was obtained just before actual smoking began, in which the largest number of particles of carbon or heavy carbonaceous vapor are heated, although none of them are heated very hot, yields the largest amount of light that can be obtained from a given burner with a given sample of gas. Such a flame, however, does not furnish the light most agreeable to the eyes.

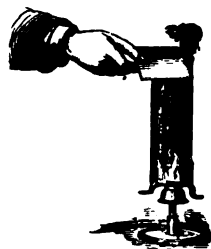


Fig. 51.

260. The flames of ordinary lamps and candles are, strictly speaking, *gas flames*.

Exp. 122. — Construct a lamp as follows: To a wide-mouthed bottle of the capacity of about 50 cc. fit a cork loosely; bore a hole in the cork, and place therein a short piece of glass tubing (No. 3) open at both ends; through this glass tube draw a piece of lamp wicking, or any loose twine, long enough to reach to the bottom of the bottle. It is essential, either that the cork should fit the bottle loosely, or that a second small hole should be bored through the cork, in order that the pressure of the external air may act upon the surface of the alcohol. To this end a very small glass tube may be inserted in the cork at some distance from the tube which carries the wick. Fill the bottle nearly full of alcohol, and after a few minutes touch a lighted match to the top of the wick. The fluid alcohol is drawn up out of the bottle by force of capillary attraction exercised by the pores of the vegetable fiber of which the wick is composed. When heat is applied to the alcohol at the top of the wick, some of it is converted into vapor; this vapor takes fire, and, in burning, furnishes heat for the vaporization of new portions of the alcohol. From the top of the wick there is constantly arising a column of gas or vapor, and upon the exterior of this conical column chemical combination is all the while going on between its constituents and the oxygen of the air. The dark central portion of the alcohol flame is nothing but gas or vapor.

Exp. 123. — Thrust the phosphorus end of an ordinary friction match directly into the middle of the flame of the alcohol lamp of Exp. 122. The combustible matter upon the end of the match will not take fire in the atmosphere of carbonaceous gases, of which the

center of the flame consists. The wood of the match stick, of course, takes fire at the point where it is in contact with the outer edge of the flame. The portion of the match in the center of the flame becomes so strongly heated during its sojourn within the circle of fire, that it is ready to inflame as soon as it comes in contact with the air; hence it is somewhat difficult to withdraw the match from the flame without its taking fire.

Exp. 124. — Hold a thin wire (best, of platinum, though iron will answer well enough) or a splinter of wood across the flame of the alcohol lamp, as shown in Fig. 52. The wire will be heated to redness, and the wood will burn, only at the outer edges of the flame where the gas and air meet. In the interior of the flame the wire will remain dark, and the wood unburned; for there is no combustion there, and comparatively little heat. If the wire be successively placed at different heights in the flame, the size and shape of the internal cone of gas can easily be made out; it will appear, moreover, that the hottest



Fig. 52.

part of the flame is just above the top of the interior cone of gas. As a rule, when glass tubing, or the like, is to be heated in a flame, it should never be placed below this point of the greatest heat.

When a candle is lighted for the first time, the cotton of which the wick is composed takes fire, and is at once consumed for the most part; but, in burning, the cotton gives off considerable heat, and some of the wax or tallow of which the candle is composed is thereby melted and converted into oil. The liquid oil ascends the wick by virtue of capillary attraction, and is converted into vapor or gas by the heat of the cotton still burning at the stump of the wick; this gas then burns precisely like the alcohol vapor in Exp. 122, § 260, and by the heat thus disengaged new portions of wax or tallow are melted. There is always a little cup of oil at the top of the rod of wax or tallow of which the candle consists, and the apparatus is as truly an oil lamp as if the oil were held in a vessel of glass or metal.

If the flame of the candle, when the snuff has become long, be blown out, a current of vapor continues to ascend from the hot wick, and this vapor may be ignited some distance above the wick. After the flame has been extinguished, the wick retains heat enough for a few moments to distill off and partially decompose a quantity of gas, although there is not heat enough generated to inflame this gas. To the gases or vapors thus evolved is to be referred the disagreeable odor which is observed when a candle is blown out. This odor may readily be prevented by thoroughly saturating the end of the wick with oil before blowing upon it, either by turning down the snuff into the melted wax of the candle, or by touching a bit of solid wax to the snuff at the moment of blowing.

Exp. 125. — Press down a piece of white letter paper for an instant upon the flame of a candle until it almost touches the wick; then quickly remove the paper before it takes fire, and observe that its upper surface is charred in the manner shown in Fig. 53. There will be obtained — in fact, burned into the paper — a diagram of the part of the flame where combustion is taking place.

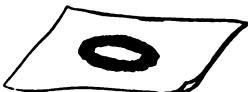


Fig. 53.

It is thus seen to be ring-shaped in section, and to inclose a space where no combustion is going on.

261. All flames, which are rendered luminous by incandescent carbonaceous particles, have the same general structure. This structure is best studied in the flame of a candle.

In the candle flame, four portions or divisions of the flame can be distinguished (Fig. 54). First, there is the small, blue, cup-shaped portion of the flame (*ab*) at the base of the wick. Here a part of the combustible gases coming from the wick are burned completely, as the oxygen of the air has free access to this part of the flame. The heat thus produced converts into vapor the oil which the wick draws up from the candle. This carbonaceous vapor rises, and forms the second part of the flame, the nonluminous cone (*c*). Here no combustion can take place. The oxygen of the air, it is true, tends to pass, by diffusion, into the interior of the flame; but, as fast as it approaches the center, it meets compounds of carbon and hydrogen in the outer portion of the flame, and enters into combination with these elements. The nitrogen of the air, however, diffuses freely into the interior of the flame, where it mixes with the combustible gases of the candle and with some carbonic acid and steam (*c*).

The third portion of the flame is the luminous zone (*d*). Here the combustion is incomplete; the gaseous compounds of carbon and hydrogen are broken up by heat into their constituent elements. The carbonaceous particles are intensely ignited, and burn to carbon monoxide, by taking oxygen from the air, and also from the carbonic acid and steam which diffuse inwards from the outermost portion of the flame.

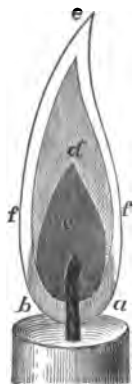


Fig. 54.

The fourth portion of the flame is the thin, scarcely perceptible, nonluminous mantle (*fef*) which surrounds the entire flame. Here the carbon monoxide and hydrogen burn to carbonic acid and steam; and, as has already been seen, a part of these gases diffuse inward, and are decomposed, furnishing oxygen for the partial combustion of the carbon in the luminous portion of the flame.

262. The principle of the **oxyhydrogen blowpipe**, as well as of the ordinary blast lamps in which air and illuminating gas are used instead of oxygen and hydrogen, is the throwing of oxygen into the combustible gas so that the combustion is intense and concentrated. On the same principle depends the use of the mouth blowpipe (Appendix, § 7).

Exp. 126. — To use the mouth blowpipe, place the open end of the tube between the lips, or, if the pipe is provided with a mouthpiece, press the trumpet-shaped mouthpiece against the lips; fill the mouth with air until the cheeks are widely distended, and insert the tip of the pipe in the flame of a candle, or of a lamp with a flat wick; close the communication between the lungs and the mouth, and force a current of air through the tube by squeezing the air in the mouth with the muscles of the cheeks, breathing, in the mean time, regularly and quietly through the nostrils. The knack of blowing a steady

stream for several minutes at a time is readily acquired by a little practice.

It is possible with the blowpipe to produce either an *oxidizing* or a *reducing* flame. When the jet of the blowpipe is inserted into the lamp or gas flame, as shown in Fig. 55, and a strong blast is forced through the tube, a blue cone of flame (*ab*) is produced, beyond and outside of which stretches a more or less colored outer cone (*ac*). The point of greatest heat in this flame is at the point of the inner blue cone; oxidation takes place most rapidly at, or just beyond, the point (*c*) of the flame, provided that the temperature at this point is high enough for the special substance to be heated.

To obtain a good reducing flame, it is necessary to place the tip of the blowpipe, not within, but just outside of, the flame, and to blow somewhat gently over rather than through the middle of the flame (Fig. 56). In this manner the flame is less altered in its general character than in the

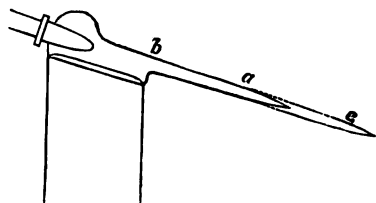


Fig. 55.

former case, the chief part consisting of a large luminous cone, con-

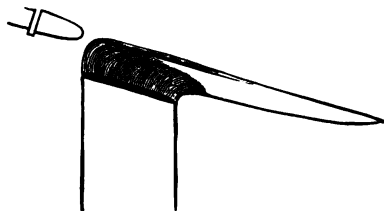


Fig. 56.

taining a quantity of free carbon in a state of intense ignition, and just in the condition for taking up oxygen. This flame is therefore reducing in its effect. The substance which is to be reduced by exposure to this flame should be completely covered up by the luminous cone, so that contact with the air may be entirely avoided.

263. Instead of forcing the air (or oxygen) into the burning fuel, the supply of air may be furnished by means of *chimneys*. Chimneys, whether of lamps or of fireplaces, are simply devices for bringing to the fuel an abundance of air, and therefore of oxygen. That in so doing they at the same time carry off the waste products of combustion, is an incidental advantage.

Exp. 127. — Light a piece of a candle 8 or 10 cm. long, and stand it upon a smooth table; over the candle place a rather tall, narrow lamp chimney of glass, the bottom of the chimney being made to rest upon the table, and observe that the candle flame will soon be extinguished. No fresh air can enter the chimney from below to maintain the chemical action, and the small quantity of air which can creep down the chimney from above is altogether insufficient to meet the requirements of the case.

Exp. 128. — Relight the candle of Exp. 127, and again place over it the lamp chimney; but, instead of allowing the chimney to rest closely upon the surface of the table, prop it up on two narrow strips of wood, so the air can have free entrance into the chimney from below. The candle will now continue to burn freely; for the heavy, cold air outside will continually press into the lower part of the chimney, and push out the warm, light products of combustion, and the candle flame will all the while be supplied with fresh air.

The direction of the current of air may be shown by placing a piece of burning *touch paper* at the foot of the chimney. Touch paper is made by soaking ordinary brown paper in a strong solution of potassium nitrate, and then drying it. On being lighted, the paper burns without flame, while emitting clouds of smoke.

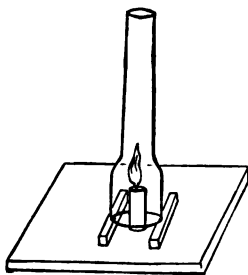


Fig. 57.

Exp. 129. — Repeat Exp. 128, and, when the candle is burning quietly, cover the top of the chimney tightly with a piece of tin or sheet iron, or with a strip of window glass. The candle will soon cease

to burn, precisely as if the chimney were closed at the bottom; for, the escape of the hot products of combustion being prevented, no air can pass into the chimney to reach the candle flame.

It is by inducing the current of fresh air (Exp. 128), or *draught*, as it is ordinarily termed, that chimneys are specially useful. Through the chimney the hot air from the lamp flows straight forward and rapidly, and of course a correspondingly direct and rapid current of fresh air presses in to supply its place. Owing to this power of rapidly supplying air, chimneys are employed upon lamps burning petroleum and other highly carbonized oils which are liable to smoke.

Exp. 130. — It is not absolutely necessary that the fresh air should flow into a chimney from below. Divide the upper part of the chimney

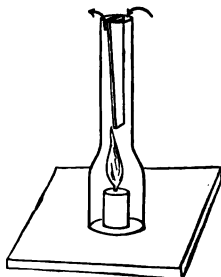


Fig. 58.

of Exp. 127 into two channels by hanging in it a strip of sheet iron or tin, as a partition at the center of the chimney (Fig. 58). Place the chimney thus divided over a burning candle, and observe that the candle will continue to burn as if in a strong draught of air, although no air can enter the chimney from below. Hold a piece of burning touch paper at the top of the divided chimney: the smoke will be drawn down into the chimney on one side of the partition, and thrown out again upon the other, as indicated by the arrows in Fig. 58. It appears from this, as well as from the tremulous motion of the

flame, that a current of cold air presses down upon one side of the division wall, and supplies the required oxygen.

264. Kindling Temperature. — In order that any combustible substance shall burn, or, in other words, in order that brisk chemical action shall occur between the combustible and the oxygen of the air, the substance must first be heated to a certain definite temperature, and subsequently maintained at that heat. The temperature at which any combustible body takes fire is known as the *kindling temperature* of that substance.

Exp. 131. — Place a small bit of phosphorus and another of sulphur, not in contact with the first, upon a fragment of porcelain 6 or 8 cm. across, and heat them slowly over the gas lamp. The phosphorus will soon take fire at a temperature of 68° to 70° ; but the sulphur will not inflame until the temperature of the porcelain support has risen to about 250° , as can be ascertained by the thermometer.

As was just now said, the degree of heat necessary to start any fire must be kept up continually, or the fire will go out. Whenever burning bodies are cooled below the kindling temperature, they are extinguished. The chemical action which occasioned the appearance of heat and light ceases.

If we pile up upon an iron grate, thick in metal, and supported in such manner that air may enter beneath it, several pieces of red-hot charcoal, the charcoal will go on burning until nearly all of it has been consumed, for the heat generated by the combustion of the portions first burned keeps up the temperature necessary to kindle the subsequent portions. If, however, we scatter about upon a cold grate several small pieces of red-hot charcoal, taking care that no two pieces of the coal shall come in contact, or be placed so as to heat one another, each of the pieces of charcoal will soon cease to burn; for the metallic grate is so good a conductor of heat that it removes heat from the isolated pieces of charcoal more rapidly than they can produce it: the temperature of the charcoal is, consequently, soon reduced to below the kindling point.

265. Precisely as coals can be extinguished by placing them upon cold metal, so flames may be put out.

Exp. 132. — Upon a ring of the iron stand place a sheet of clean wire gauze about 10 cm. square; lower the ring so that the gauze shall be pressed down upon the flame of a lamp or candle almost to the wick, as shown in Fig. 59. No flame will be seen above the gauze, but instead of flame a cloud of smoke. The gauze is a mere open sieve; there is nothing about it which can prevent the gas, which was just now burning with flame above the wick of the candle, from passing through. Indeed, it may be seen from the smoke, that the particles of carbon which, in the original undisturbed flame, were becoming incandescent, and so affording light, do now actually come through the gauze.



Fig. 59.

The explanation of the phenomenon is simply that the metallic sieve conducts away so much heat, that the temperature of the candle flame is reduced to below the kindling point. That this is really so, is proved by the fact, that after the gauze has become sufficiently heated by long-continued contact with the flame below, — after it has attained the kindling point of the candle gas, — it will no longer extinguish the flame. In like manner a candle flame may be cooled to such an extent that it will go out, by placing over it a small coil of cold copper wire; while, if the wire be previously heated, the flame will continue to burn.

If the smoke of unburned gas which has passed through the cold wire gauze be touched with a lighted match, and so brought to the kindling temperature, it will burst into flame.

The power of wire gauze to prevent the passage of flame has been usefully applied in several ways, notably for the prevention of explosions in those coal mines which are liable to accumulations of marsh gas (§ 272). For this purpose, safety lamps, one form of which is shown in Fig. 60, are constructed by inclosing an ordinary oil lamp completely in wire gauze, so that the flame within the gauze will not kindle any combustible or explosive gas into which it may be carried. In case such a lamp be carried into a place filled with explosive gas, the latter will, of course, pass into the lamp through the meshes of the gauze, and burn within the cage. This combustion gives warning of the presence of the dangerous gas, and indicates to the workman that he should withdraw from the locality; the mine may then be ventilated.



Fig. 60.

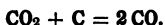
Exp. 133.—Beneath a sheet of wire gauze resting on a ring of the lamp stand, place an unlighted Bunsen's burner, at such a distance that the gauze shall be 3 or 4 cm. above the top of the lamp; turn on the gas and light it above the wire gauze. It will continue to burn on top of the gauze for an indefinite period; for the gauze will, in this case, always be kept cool by the cold gas which is continually passing through

it. Carefully and gradually lift the ring which carries the gauze, and determine how far it is possible to lift the gauze above the gas jet without extinguishing the flame.

An effect somewhat similar to that produced by wire gauze is often seen in ordinary fires. When a mass of red-hot anthracite, charcoal, or coke is burning freely upon a grate in the open air, there is always a blue flame of carbon monoxide burning above the coal. This gas results from the reduction of carbonic acid by means of hot carbon, as already stated. Air enters at the bottom of the grate, and combines with the hot coal which it finds there, to form carbon dioxide (CO_2). This carbon dioxide, as it rises through the hot coal in the middle of the fire, is deprived, by the heated carbon, of half its oxygen,—



Fig. 61.



The carbon monoxide, being combustible, will at once take fire on coming in contact with the air, provided the temperature at the summit of the fire be equal to the kindling temperature of this gas. But, if the temperature of the fire is in any way reduced below this point, as, for example, by throwing on too large a quantity of cold fuel, which is, of course, equivalent to covering the fire with a sheet of wire gauze, then the carbon monoxide will be extinguished, and, escaping into the chimney, will produce no useful effect.

The temperatures at which combustibles take fire are ordinarily lower than the temperatures of their flames; i.e., than the temperature produced by the combustion. There is a marked exception to this rule in the case of nitrogen, which is really a combustible gas, though not readily to be kindled. At very high temperatures, such as are produced by powerful electric currents, nitrogen burns in the air with a visible flame and production of nitrous and nitric acids. This flame does not set fire to the air, or spread throughout the atmosphere, to the destruction of all living things, because the kindling point of nitrogen is higher than the heat of its flame.

266. Carbon and Sulphur. — *Carbon disulphide* (CS_2) is interesting from its correspondence to carbon dioxide (CO_2), and forms another instance of the analogy between the compounds of oxygen and sulphur. Carbon disulphide is prepared by passing the vapor of sulphur over red-hot charcoal. It is a colorless, strongly refracting liquid, which boils at about 54° , and evaporates rapidly at the ordinary temperature of the air. It possesses an ethereal odor when purified, but the common disulphide has a peculiar and very disagreeable smell. It is very inflammable, and burns with a blue flame, the product of the combustion being carbonic and sulphurous anhydrides. Hence, by simply burning it in a lamp, with proper precautions, it may be made to serve as a convenient germicide or disinfecting agent, as in the case of fumigating rooms which have been occupied by persons suffering from certain infectious diseases. Carbon disulphide is not soluble in water, but it is easily soluble in alcohol, and is itself a powerful solvent of fats and various other substances. It is used in the arts as a solvent of phosphorus and sulphur, and is employed in the cold process of vulcanizing caoutchouc. Its vapor is much heavier than air (§ 286); hence the use of the disulphide in some countries for suffocating vermin, such as rabbits and ground squirrels.

CHAPTER XVII.

CARBON (continued).

267. Carbon unites with hydrogen, oxygen, and nitrogen, or with two of these elements, or with all three of them, in the most varied proportions, to form numberless compounds, some of which are extremely complex. There are more compounds of carbon now known than of all the other elements put together. Since many of the more complex compounds of carbon occur ready formed in animals and plants, or are produced by the transformation of substances derived from these sources, they are usually classed together and studied under the head of Organic Chemistry.

There is no sufficient reason, chemically speaking, for making this division, since chemical compounds, whether derived from the animal, vegetable, or mineral kingdoms, are governed by the same laws. It is, in fact, impossible to draw any sharp line of demarcation between organic and inorganic chemistry; still, on account of the vast number of the carbon compounds, the mere names of which would fill a volume, this arrangement has the merit of convenience. In this and the two following chapters a few of the more important of these so-called organic bodies will be considered.

Other elements beside those already mentioned, such as sulphur and phosphorus, may enter into the composition of these bodies. For example, several of the complex substances which exist in the bodies of animals, such as albumin and the matter which forms the substance of the hair, contain sulphur as an essential ingredient. Moreover, there are numerous *organic acids* which form salts of the various metals, and many of these salts exist ready formed in nature. Since a very large proportion of the compounds of carbon contain hydrogen, and most others can be shown to be derived from the compounds of carbon and hydrogen known as *hydrocarbons*, by the replacement of one or more atoms of hydrogen by other atoms or groups of atoms, what is usually called Organic Chemistry may properly be defined as *the chemistry of the hydrocarbons and their derivatives.*

268. **Carbon and Nitrogen.**—Prominent among the compounds of carbon and nitrogen is *cyanogen* (**CN**), which is an important compound radical, and which also exists in the free state.

269. **Cyanogen (CN or Cy).**—Carbon and nitrogen do not unite directly, but, when a current of nitrogen is passed over red-hot charcoal which has been previously soaked in a solution of potassium carbonate, there is formed potassium cyanide, a compound containing the radical cyanogen, —

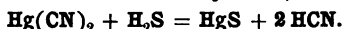


Free cyanogen is best prepared by heating mercuric cyanide, thus:—



It is a colorless, poisonous gas of suffocating odor and ready inflammability. Its molecule contains two atoms of the radical, and is written (**CN**)₂.

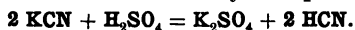
270. **Hydrocyanic acid (HCN)** may be prepared by passing hydrogen sulphide over mercuric cyanide, —



It is a combustible and volatile liquid, possessing the odor of bitter almonds, and is intensely poisonous. In aqueous solution it is known as *prussic acid*.

Cyanogen and hydrocyanic acid are analogous in many ways to chlorine and hydrochloric acid. The *cyanides* may well be classed as halides. There are numerous cyanides and double cyanides, and several of them are of great practical importance. Some of them will be mentioned under the head of the different metallic elements. Normal, simple cyanides correspond in composition to the chlorides, the univalent radical (§ 180) **CN** occupying the place of **Cl**. Thus potassium cyanide is **KCN**; zinc cyanide is **Zn(CN)**₂.

Exp. 134.—To a *very minute* quantity of solid potassium cyanide add a few drops of strong sulphuric acid. The effervescence which takes place is due to the escape of hydrocyanic acid, which may be recognized by its peculiar odor. The reaction is similar to that which takes place when common salt is treated with sulphuric acid in the production of hydrochloric acid. It may be expressed as follows:—



The *cyanates* correspond to *cyanic acid* (**HCNO**). Thus potassium cyanate is **KCNO**.

Bodies known as *sulphocyanates*, such as NH_4CNS (ammonium sulphocyanate), derived from sulphocyanic acid, are also known.

271. **Compounds of carbon and hydrogen, or hydrocarbons**, are very numerous. We first consider one of the most familiar of them, *marsh gas*.

272. **Methane, or Marsh Gas (CH_4)**. — In hot summer weather bubbles of gas are often seen rising to the surface of stagnant pools. If a pole be thrust into the mud at the bottom of the pool, a considerable amount of the gas will rise, and may be collected by holding an inverted bottle full of water over the ascending bubbles. The gas thus collected contains a certain amount of carbon dioxide (which may be removed by putting some milk of lime into the bottle, and shaking it for a short time), together with a little nitrogen; the greater part, however, consists of a colorless gaseous compound of carbon and hydrogen, very properly known as *marsh gas*. It is a product of the decay of vegetable matter under water, where the supply of air is insufficient to oxidize the whole of the organic matter to carbon dioxide and water.

273. Methane forms a very considerable portion of ordinary illuminating gas made by distilling coal. From some varieties of bituminous coal it is disengaged at the ordinary temperature, and forms the *fire damp* of coal mines. Like hydrogen, it forms an explosive mixture with air, and the explosion of this mixture in badly ventilated mines is often the cause of frightful loss of life. The gas may be prepared artificially as follows: —

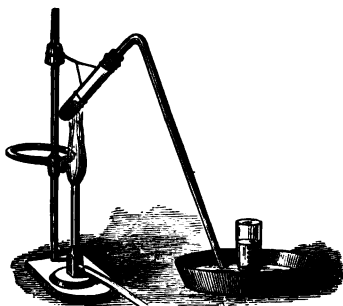
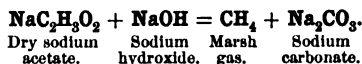


Fig. 62.

Exp. 135. — Mix together 2 g. of crystallized sodium acetate, 4 g. of sodium hydroxide, and 8 g. of calcium hydroxide. Heat the mixture gently upon an iron plate, until all

the water of crystallization of the acetate has been expelled, and the mass has become dry and friable. Charge an ignition tube, 20 cm. long, with the dry powder, heat it above the gas lamp, and collect the

gas at the water pan. Marsh gas is evolved from the mixture at a temperature below redness, and a residue of sodium carbonate is left in the ignition tube. The purpose of the lime is to render the mass porous and infusible, or nearly infusible, so that the tube may be heated equably. The reaction may be represented as follows:—



Another method is by passing a mixture of hydrogen sulphide and carbon disulphide vapor over red-hot copper turnings,—



This method is especially interesting, as it shows how readily marsh gas may be made synthetically from its elements. Both carbon disulphide and hydrogen sulphide may easily be prepared by causing their elements to combine.

274. Marsh gas is transparent, colorless, and little more than half as heavy as air. Next to hydrogen, it is the lightest known substance, its specific gravity being only 8. It takes fire readily when touched with a lighted match, and burns with a bluish yellow flame.

275. That marsh gas really contains hydrogen and carbon, may readily be proved by bringing into play, under appropriate conditions, the strong affinity of chlorine for hydrogen.

Exp. 136.—Fill a tall bottle, of at least 1 l. capacity, with warm water; invert it over the water pan, and pass marsh gas into it, until a little more than one third of the water is displaced; cover the bottle with a thick towel, to exclude the light, and then fill the rest of the bottle with chlorine. Cork the bottle tightly, and shake it vigorously, in order to mix the gases together, keeping the bottle always covered with the towel. Finally open the bottle, and apply a light to the mixture. Ignition takes place, hydrochloric acid is produced, while the sides and mouth of the bottle become coated with solid carbon in the form of lampblack. The presence of the acid may be proved by the smell, by its reaction with moistened blue litmus paper, and by the white fumes which are generated when a rod moistened with ammonia water is brought in contact with the escaping acid gas.

276. **Chloroform** (CHCl_3).—When chlorine is allowed to act slowly on marsh gas, one or more products are obtained, according to the

length of time the action continues, their composition being represented by the formulas CH_3Cl , CH_2Cl_2 , CHCl_3 , and CCl_4 , known respectively as *monochlor-*, *dichlor-*, *trichlor-methane* (or chloroform), and *carbon tetrachloride*. This replacement of hydrogen by chlorine is an example of what is known as *substitution*, and these products are spoken of as *the chlorine substitution products of methane*. Chloroform (CHCl_3) may thus be regarded as marsh gas, in which three atoms of hydrogen have been replaced by three atoms of chlorine. It is manufactured in practice by distilling dilute alcohol, or sometimes a mixture of acetone and dilute alcohol, with bleaching powder. Water and chloroform come off together, but do not mix in the receiver: the chloroform, being the heavier, sinks to the bottom, and may be withdrawn and purified. Chloroform is a colorless, volatile liquid, the vapor of which, when inhaled, causes temporary insensibility to pain, and on this account it is used in surgical operations. Iodine and bromine substitution products also can be obtained. Iodoform (CHI_3) is a valued medicament.

277. Illuminating Gas.—The principle involved in the manufacture of illuminating gas has already been illustrated in Exps. 102 and 103. Illuminating gas is ordinarily prepared by subjecting coal or petroleum to processes of destructive distillation (§ 234). Many other substances, made up wholly or in part of compounds of hydrogen and carbon, such as oil, wood, resin, peat, and even bones, have been used for making illuminating gas at one time or another. Fig. 63 shows, in a general way, the processes involved in the manufacture and purification of coal gas.

The coal is introduced into the retorts *C*, which are cylindrical or semicylindrical tubes of clay or iron, arranged in sets of three or five, or even more, and heated by a coke fire burning on the grate bars *A*. All the products of the distillation, except the coke which remains in the retort, are volatile at the high temperature employed, and pass up the vertical standpipe *T*. The relative proportions of these products, and to a certain extent their character, depend on the quality of coal employed, and on the temperature at which the distillation takes place. It may, however, be said, in general terms, that these products, when cooled to the ordinary temperature, are of three kinds,—solid, liquid, and gaseous.

The gases obtained by the distillation of coal are marsh gas, carbon monoxide, and hydrogen, together with the vapor of various hydrocarbons to be mentioned directly, as well as carbon dioxide, nitrogen, aqueous vapor, and hydrogen sulphide. The liquid portion of the dis-

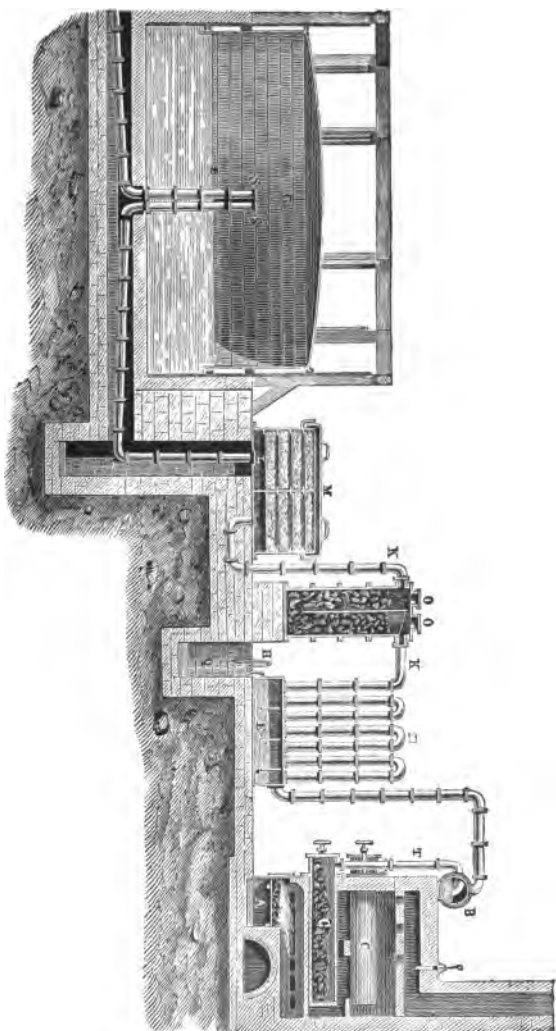


Fig. 63. — Manufacture of Coal Gas.

tillate consists of an aqueous solution of ammonium salts, notably carbonate, sulphide, and sulphocyanate of ammonium, certain liquid hydrocarbons, such as benzene, toluene, etc., which will be considered hereafter (§ 342), and a semiliquid or viscous tar. The solid product of the distillation of coal is the coke left in the retort.

In the production of gas, all the volatile products of the distillation go up the standpipe *T*, which is curved at its upper extremity, and dips into water in the hydraulic main *B*. In this water a portion of the tar and aqueous vapor is condensed, and the ammoniacal salts are, in part, dissolved. The gas then passes alternately up and down through the cooling pipes *D*, called the *condensers*, and suffers further condensation, the remaining tar and the liquid hydrocarbons being deposited. The gas is often further purified by passing through a tower, *O*, filled with fragments of coke, over which water trickles, the water absorbing the ammoniacal salts still present. The gas then passes through the purifier *M*, where it comes in contact with slaked lime, and is freed from hydrogen sulphide and most of its carbon dioxide, and thence into the gas holder *G*. The lime in the purifiers is sometimes replaced wholly or in part by dry ferric hydroxide, which decomposes the hydrogen sulphide and retains the sulphur.

278. After purification, the gas, as delivered to the consumer, consists mainly of marsh gas, hydrogen, and carbon monoxide; the marsh gas usually amounting to about one third part of the whole gas. These nonluminiferous, or very feebly luminiferous, gases serve as carriers of the six or seven per cent of real light-producing ingredients which are contained in the gas. This mixture of light-giving ingredients is exceedingly complex. The vapor of benzene (C_6H_6), no doubt, plays a prominent part. Some of the higher members of the marsh-gas series lend their aid, and a hydrocarbon of composition C_2H_2 , called *acetylene*, is important and very generally present. Sometimes a little olefiant gas (C_2H_4) is present; but the old view, that this substance constitutes the chief luminiferous ingredient of coal gas, is no longer admitted.

The coal tar obtained as a waste product in the gas manufacture is a very complex substance. Among other substances, it contains benzene or benzol, used in the manufacture of anilin colors, and anilin itself in very small proportion. From it is obtained pitch also.

279. Marsh gas, or methane (CH_4), is the first of a series of hydrocarbons, known as the *marsh-gas series*, the members of

which are not readily acted upon by the ordinary chemical agents, such as hydrochloric, nitric, and sulphuric acids, etc., and are incapable of forming *addition products* (§ 180).

On arranging these hydrocarbons in a series in accordance with the number of carbon atoms contained in their molecules, as in the following table, where eight of some thirty-five which are known to exist are given, —

| Name. | Formula. | Boiling Point. |
|----------------------------|--|----------------|
| Methane or Methyl Hydride, | $\text{CH}_4 = \text{CH}_3 \cdot \text{H}$ | [a gas] |
| Ethane “ Ethyl “ | $\text{C}_2\text{H}_6 = \text{C}_2\text{H}_5 \cdot \text{H}$ | [a gas] |
| Propane “ Propyl “ | $\text{C}_3\text{H}_8 = \text{C}_3\text{H}_7 \cdot \text{H}$ | [a gas] |
| Butane “ Butyl “ | $\text{C}_4\text{H}_{10} = \text{C}_4\text{H}_9 \cdot \text{H}$ | 8° |
| Pentane “ Amyl “ | $\text{C}_5\text{H}_{12} = \text{C}_5\text{H}_{11} \cdot \text{H}$ | 38° |
| Hexane “ Hexyl “ | $\text{C}_6\text{H}_{14} = \text{C}_6\text{H}_{13} \cdot \text{H}$ | 68° |
| Heptane “ Heptyl “ | $\text{C}_7\text{H}_{16} = \text{C}_7\text{H}_{15} \cdot \text{H}$ | 98° |
| Octane “ Octyl “ | $\text{C}_8\text{H}_{18} = \text{C}_8\text{H}_{17} \cdot \text{H}$ | 128° |

it will be noticed, on comparing the formulas given, that each member of the series differs in composition from the preceding by an atom of carbon and two atoms of hydrogen (CH_2). Thus, if CH_2 be added to the formula of methane, the formula of ethane is obtained; and if CH_2 be added to the formula of ethane, that of propane is formed; etc. Any series of this kind, the members of which have an analogous constitution, and differ in composition from each other by CH_2 or some multiple thereof, is called an *homologous series*; and the substances constituting such a series are said to be *homologues* of each other.

For any such homologous series, a general formula can be devised, which will apply to each member of the series. Thus the general formula of the marsh-gas series of hydrocarbons is $\text{C}_n\text{H}_{2n+2}$. If $n = 1$, the formula becomes CH_4 ; if $n = 3$, the formula becomes C_3H_8 , that of propane; and so on.

In like manner the members of any class of derivatives formed from an homologous series of hydrocarbons by the replacement of atoms of hydrogen by other atoms, or groups of atoms, will differ from each other by CH_2 or some multiple thereof, and will form homologous series of compounds, several examples of which will be given presently. The marsh-gas series is but one of a number of homologous series of hydrocarbons.

280. The generally accepted view of the cause or nature of homology is based upon the valence theory. The maximum valence of carbon being four, an atom of this element can hold

in combination four atoms of hydrogen, forming a saturated molecule. Thus the molecule of marsh gas is *saturated*: it cannot take on anything; it cannot unite with other atoms or groups of atoms to form addition products. If this view is correct, two molecules of marsh gas cannot unite to form a new molecule, all the atom-fixing powers of the atoms of carbon and of hydrogen being exhausted; but two unsaturated groups, formed by the removal of an atom of hydrogen from *each of two molecules* of marsh gas, can readily unite: thus CH_3 can unite with CH_3 to form a molecule of ethane (C_2H_6).

To represent the matter graphically, the formula of methane is

written $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$ (for we have reason to believe that the atoms of

hydrogen are of equal chemical value, i.e., bear the same relation to each other and to the rest of the molecule, since but one monochlormethane (CH_3Cl) is known); and if an atom of hydrogen be removed, we obtain

$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C} \\ | \\ \text{H} \end{array}$ (Methyl), i.e., an unsaturated group of atoms, which, while

apparently incapable of a separate existence, has a valence of one, and can combine with another similar group to form a saturated molecule

of ethane, $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$, the carbon atoms apparently having the power

to unite with each other. Applying the same course of procedure, and removing an atom of hydrogen from the molecule of ethane, we should have a univalent radical C_2H_5 (ethyl), capable of combining again with another univalent radical (methyl, for example): thus $\text{C}_2\text{H}_5 - \text{CH}_3$ would form a molecule of the third member of the series, C_3H_8 (propane).

A reaction by which ethane can be formed from methane well illustrates this step-by-step building-up of the members of an homologous series. If methyl iodide is treated with metallic sodium under proper conditions, sodium iodide and ethane result, according to the reaction —



the sodium removing the atoms of iodine, and leaving the two univalent groups of atoms free to unite with each other; or, again, the fol-

lowing reaction takes place, if, instead of only methyl iodide and sodium, we employ methyl iodide, ethyl iodide, and sodium, propane being formed.



This method has been largely employed by chemists in the preparation of the higher members of the series.

Methane may be regarded as a compound of hydrogen (H) with the group of atoms CH_3 , called methyl; and this group, like the group NH_3 (ammonia), can take part in many chemical transformations as if it were a single atom; similarly the other members of this series may be regarded as *hydrides* of univalent compound radicals, as indicated by the symbols and names of the table. Beside forming hydrides, this group of atoms enters into a variety of other compounds, replacing hydrogen, atom for atom, or acting as a univalent radical.

It will be observed, that, while each member of the marsh-gas series differs from the preceding one by CH_2 , there is a difference of 30° in the boiling points of successive members. The specific gravity and other physical properties show a corresponding and regular increase or decrease. As regards chemical properties, it may be said that there is a close resemblance between the several members of the series. In general, what one will do, all will do; the difference in chemical properties being one of degree of action rather than of kind. Indeed, this remark is true of all the homologous series of hydrocarbons known: the members of any series resemble each other more closely in chemical properties than they resemble the members of any other series. Several of the hydrocarbons of this series occur in the more volatile portions of the *coal oil* obtained by distilling bituminous coals and shales at low temperatures, and in *petroleum naphtha* also.

281. *Petroleum* (literally, "rock oil") is a not uncommon natural product found in various parts of the world. In some cases it rises to the surface of the earth, but it is generally obtained by sinking wells into the rock strata in which it occurs. On this continent it is already found in large quantities in Pennsylvania, Ohio, and Canada. In some of the wells the oil rises to the surface, being forced out by the marsh gas which accompanies it; in other cases the oil does not reach the surface, and must be pumped out.

282. *Petroleum* is a thick, greenish, oily liquid, of somewhat varying composition. That from Pennsylvania yields, on distillation, a quantity of light, volatile naphtha called *gasolene*, and

benzine, as well as an illuminating oil known as *kerosene*, and a heavy lubricating oil, which holds in solution more or less paraffin (§ 320). The lubricating oil is not so well fitted as kerosene to be burned in lamps, because it has less capillary power: it does not rise in the lamp wick so readily as the lighter oil does.

283. **Kerosene** and **Gasolene** consist chiefly of members of the marsh-gas series of hydrocarbons, from C_4H_{10} to $C_{12}H_{26}$, together with a small proportion of members of the "aromatic series" of hydrocarbons (§ 342).

By subjecting the heavy, less volatile oils of petroleum to strong heat under fit conditions, the complex molecules of which they are composed may be split up into simpler molecules. This process, technically known as *cracking*, is put to practical use in petroleum refineries for obtaining kerosene through the decomposition of paraffin and the lubricating oils. Besides kerosene, a certain proportion of the lighter and less valuable gasolene is produced by the cracking.

In order that kerosene may be safely burned in lamps, it is important that it should not contain too large a proportion of the most volatile members of the mixture known as gasolene or benzine; for the vapors of these naphthas are highly inflammable, and mixtures of them with air may explode with extreme violence. Such explosive mixtures are specially liable to form in lamps and cans which are only partially filled with poorly refined kerosene. They may form also slowly above large surfaces of the fairly well refined material when it is left to itself for some time in partially emptied tanks, barrels, or cans.

On account of the danger of explosion and fires, laws have been passed in many states to control the character of the kerosene sold for illuminating purposes. Most of these restrictions relate to what is called the *flashing point* of the oil, or the temperature at which inflammable vapor is given off from it. Various forms of apparatus have been devised for determining the flashing point.

A simple form is shown in Fig. 64. The cylinder *a* is 3 cm. in diameter, and about 10 cm. long. A glass tube, *c*, contracted to a small orifice, *b*, passes through the wooden plug

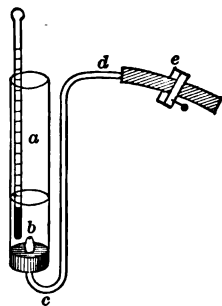


Fig. 64.

which closes the lower end of the cylinder. At *d* the tube is connected with a source of compressed air, the flow of which can be controlled by a compression cock, *e*. The cylinder *a*, having been about one third filled with the kerosene to be tested, is secured in a clamp, and immersed in a water bath to the level of the oil. Air is then passed through the tube *dcb*, *e* being so adjusted that a layer of foam about 5 cm. thick shall be formed on the surface of the oil. The bulb of a thermometer is immersed in the oil, and this instrument will indicate the temperature of the liquid. From time to time, as the temperature of the water bath rises, a light should be touched to the top of the cylinder. When the oil has become heated to the flashing point, the vapor from it will take fire, and a flash of flame will pass down to the surface of the oil. In several states the legal flashing point is $44^{\circ}\text{C.} = 111^{\circ}\text{F.}$

284. Marsh gas itself, as has been stated, accompanies petroleum, and in some localities, notably in Pennsylvania and in New York State, it issues from the ground in enormous quantities. In many places the so-called gas wells supply an abundance of fuel not only for lighting and heating houses and cities, but for carrying on great metallurgical and manufacturing operations.

285. If air is made to pass through the light naphtha of petroleum (gasolene), or if the naphtha is made to evaporate into a confined space, the air will become charged with inflammable vapor, and may be burned like ordinary coal gas. Gas machines constructed on this principle have been in use for many years in country houses. Similarly, the nonluminous water gas obtained by passing steam through hot coal or coke, and consisting mainly of a mixture of marsh gas and carbon monoxide, is rendered of illuminating value by enriching or *carburetting* it, as the term is, by incorporating with it vapors of naphtha. A serious objection to the use of water gas is due to the highly poisonous character of the carbon monoxide which is contained in it. Petroleum naphtha (benzine) is much used as a solvent, notably by dyers and scourers. It is used by painters also as a substitute for oil of turpentine.

Exp. 137. — Into a small bottle containing several teaspoonfuls of benzine put a bit of tallow; close the bottle and shake it; the fat is completely dissolved.

286. It is to be observed that the vapors of all the petroleum products, even those known in technical language as *light stuffs*, are heavier

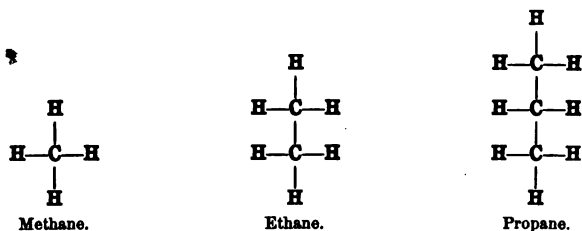
than air. This fact may readily be made manifest by a very simple calculation. If, for example, we consider the vapor density of heptane (C_7H_{16}), which is equal to one half the molecular weight (§ 170), it will appear that it is equal to 50, whereas air is only about 14.5 times heavier than hydrogen (§ 39). But $14.5:1 = 50:(x = 3.4)$; that is to say, heptane vapor is nearly $3\frac{1}{2}$ times heavier than air, and it may readily be decanted from one vessel to another, like carbon dioxide. Another heavy vapor is that of carbon disulphide (§ 266). The vapor density of this substance is 38; and, on dividing this number by 14.5, it appears that the vapor is 2.6 times heavier than air. Marsh gas, on the contrary, is much lighter than air. The molecule of CH_4 weighs 16, and the vapor density is 8, which, on being divided by 14.5 (the vapor density of air), gives as a quotient 0.551.

287. Isomerism. — One of the most important consequences of the fact that compounds of carbon have the power of uniting with one another with great facility (§ 279) is, that numberless bodies are formed which are found on analysis to have precisely the same percentage composition, although differing, it may be very widely, in respect to their physical and chemical properties. Such bodies are said to be *isomeric* (*ἴσος*, "equal"; and *μέρος*, "part"): and the differences which they exhibit are supposed to depend upon differences in their molecular structure; i.e., the same atoms or groups of atoms are differently arranged in the unlike molecules, and do not stand to each other in the same relations. Moreover, the state of aggregation of the elementary atoms in the compound molecules may be so different, that the groups of atoms in which they occur may be regarded as of different kinds; as when, for example, one substance contains two atoms of carbon (C_2) in a certain relation to each other as an essential constituent, and another substance, isomeric with it, contains six atoms of carbon (C_6), which bear to one another a relation closely analogous to that of the two carbon atoms in the first substance.

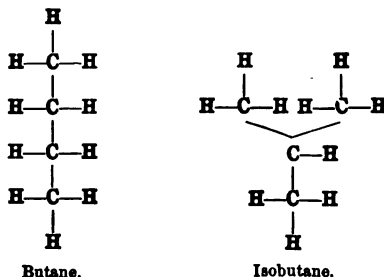
Two classes of *isomerides* are distinguished: the term *metamerism* (*μετά*, "change"; and *μέρος*, "part") being used to designate compounds which have the same molecular weight as well as the same percentage composition, although they may belong to classes of bodies of essentially different character and structure; while the term *polymerism* (*πολύς*, "many") applies to compounds having different molecular weights and the same percentage composition. It is noteworthy that

substances differing as widely in their chemical properties as acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) and grape sugar ($\text{C}_6\text{H}_{12}\text{O}_6$) are isomeric. So, too, the formula $\text{C}_2\text{H}_6\text{O}$ represents the composition of the molecules of two bodies of very different properties, one being a primary alcohol (§ 305), and the other an ether (§ 306). Yet again, the compounds known as *allyl alcohol* and *dimethyl ketone* both have the formula $\text{C}_3\text{H}_6\text{O}$: they are metameric bodies.

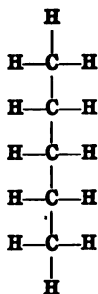
The marsh-gas hydrocarbon known as *butane* (C_4H_{10}) will give us a good illustration of metamerism. We have seen (§ 280) how the members of this series of hydrocarbons can be formed from each other by the replacement of a hydrogen atom by the methyl group CH_3 . It can readily be seen from the structural symbols of the first three members of this series that no isomers are possible if produced by a different grouping of the carbon atoms; for these symbols represent the only possible way in which, upon the valence theory, the atoms composing the molecules can be united:—



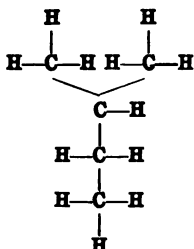
As was stated in § 280, the fourth member, butane, is derived from the third, propane, by methyl (CH_3) taking the place of an atom of hydrogen. Now, this substitution can either take place in one of the methyl groups of propane or in the CH_2 group: consequently two bodies of different structure, but having the same composition, are possible. Two, and two only, are known, which are called *butane* and *isobutane*:—



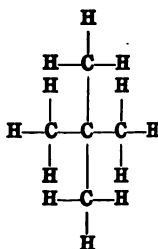
Of the fifth member, similarly, three isomeric forms are possible, which also are known :—



Pentane.



Isopentane.

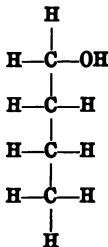


Trimethyl methane.

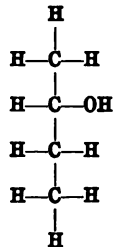
288. It would lead us too far to consider the reactions upon which these structural formulas are based. When the number of carbon atoms is increased, the number of possible isomers increases rapidly; there are eighteen possible hydrocarbons of the marsh-gas series, having the formula C_5H_{12} . To determine the maximum number of possible isomerides of a given formula is a purely mathematical problem.

The marsh-gas hydrocarbons of structure like the first formula of butane, and containing no carbon atoms directly acting upon more than one other carbon atom, are called the *normal marsh-gas hydrocarbons*, and the boiling points in the table (§ 279) refer to these bodies.

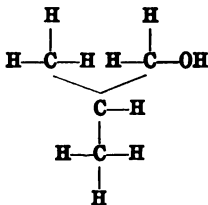
As all carbon compounds may be regarded as derived from hydrocarbons by atoms or groups of atoms taking the place of hydrogen, and this replacement may be of hydrogen in different positions in the molecule, the number of possible isomeric compounds is very large; for example, there may be four isomeric hydroxyl substitution products of the composition $\text{C}_4\text{H}_9\text{OH}$, according to which of the hydrogen atoms are replaced in the butanes, as represented in the structural formulas—



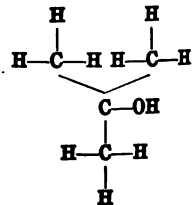
Butyl alcohol.



Secondary butyl alcohol.



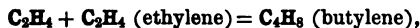
Isobutyl alcohol.



Tertiary butyl alcohol.

289. A good example of polymerism is seen in the case of the two substances, acetylene (C_2H_2), which is a gas possessing peculiar and characteristic properties, and benzene (C_6H_6), which is a volatile liquid that solidifies like water at 0° . Here the molecules of the two bodies are manifestly of different degrees of complexity. Numerous instances of polymerism occur in some homologous series, such, for example, as in the olefines (§ 335), and in the series of which acetylene (C_2H_2) is the first member. In other homologous series, on the contrary, polymerism is absent, while examples of metamerism are abundant, as is the case, indeed, in the marsh-gas series just now described (§ 279).

With regard to polymerization, it may be said to occur whenever two or more similar molecules combine to form a single molecule, as when two molecules of NO_2 (nitrogen peroxide) unite to form the molecule N_2O_4 (nitrogen tetroxide, § 57); whereas, when unlike molecules combine, the act is said to be one of addition: thus, we have polymerization when two molecules of ethylene are condensed to one of butylene,—



and *addition* when the unlike molecules ethylene and chlorine unite, as in the following reaction:—



Strictly speaking, bodies are polymerides only when their molecular weights are multiples or submultiples one of the other. Polymerization is often induced by the action of heat, whereby several comparatively simple molecules are *condensed* into one more complex molecule. Indeed, the phenomena of polymerism are closely analogous to those of allotropism (§ 172); though the latter term is commonly restricted to cases of the polymerization of *elements*, as when several atoms of oxygen condense to form ozone, or atoms of phosphorus unite to form red phosphorus, or atoms of sulphur to form the several allotropic modifications of sulphur, and so on.

290. **Alcohols.**—As has already been stated, the marsh-gas radicals, beside forming hydrides, enter into a variety of other compounds in which they are united with other atoms or groups of atoms. Among these compounds are the hydroxides called *alcohols*. These bodies may be regarded as water in which one atom of hydrogen is replaced by the hydrocarbon radical, or as formed by the union of the hydrocarbon radical and the hydroxyl group. They correspond to the hydroxides of such elements as sodium and potassium, bodies already somewhat familiar.

H—OH
Water.

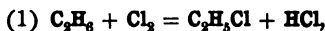
K—OH
Potassium hydroxide.

Na—OH
Sodium hydroxide.

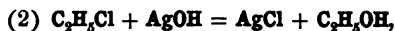
CH₃—OH
Methyl hydroxide.

C₂H₅—OH
Ethyl hydroxide.

The hydroxides of the radicals may be obtained from the corresponding hydrocarbons, in a somewhat indirect manner, by methods which indicate their structure and relation. For example, one method by which ethyl hydroxide can be obtained is shown by the following reactions:—



where an atom of chlorine is seen to replace an atom of hydrogen in ethane, with formation of ethyl chloride; and



in which the ethyl group, by replacing an atom of silver, unites with hydroxyl, which may thus be said to have replaced, or been substituted for, an atom of hydrogen in ethane. Both these reactions are much used by chemists for obtaining the hydroxides of the higher members of the marsh-gas series. Ethyl hydroxide is ordinary alcohol (**C₂H₅OH**), this formula representing the strongest absolute alcohol.

291. Alcohol (C₂H₅OH).—When the juices of plants or of fruits containing sugar, such as the juice of the grape, are kept for some time at a temperature of 20°, a peculiar change takes place. The liquor begins to *work*; bubbles of carbon dioxide (CO₂) are given off; and it will be found, finally, that the sweet taste of sugar has disappeared, and that the solution now has a new smell and taste.

The fermentation is caused by microscopic organisms, which feed upon the constituents of the grape juice, and consume the oxygen of the sugar in such manner that the sugar suffers decomposition, and is split up into carbon dioxide and alcohol. The ferment organisms were either attached to the outside of the fruit, or their spores or *germs* fell from the air into the juice. Multitudes of such spores float about in the air. Similar changes may readily be brought about in a weak solution of glucose or in diluted molasses, by means of ordinary

yeast (Exp. 117, § 249), which is nothing more than an agglomeration of a microscopic plant of extremely simple structure. It is a kind of fungus which grows rapidly in the fermenting liquor.

292. Ethyl alcohol is a colorless, volatile, and inflammable liquid, lighter than water, and capable of mixing with it in all proportions.

The volatility and inflammability of alcohol have already been illustrated in Exp. 122, § 260. The production of alcohol as a result of fermentation may be illustrated by a repetition of Exp. 117, § 249, under somewhat different conditions, as follows:—

Exp. 138.—Dissolve 50 g. of glucose sirup or of thick molasses in 400 cc. of water, and with the solution fill a flask of 350 or 400 cc. capacity nearly to the neck. Crumble into the liquid a bit of compressed yeast as large as a pea, and connect the flask with a bottle filled with water, as represented in Fig. 65. Put the whole apparatus in a warm place. Fermentation will soon set in, and bubbles of carbonic acid will be seen rising through the liquid. As this gas collects in the upper part of the flask, it will pass over into the small bottle, and force out a corresponding amount of water.



Fig. 65.

When the bottle is full or partly full of the gas, remove the stopper, and prove the presence of carbon dioxide, either by means of a burning match, which will be extinguished (Exp. 113, § 246), or by means of limewater, which will be rendered turbid (Exp. 110, § 244). Allow the liquid in the flask to remain in a warm place for about 48 hours, when the sweet taste of the sugar will be found to have well-nigh disappeared, as the sugar will have been converted mainly into alcohol and carbonic acid.

293. To separate the alcohol from the liquid in which it has been formed by fermentation, the liquid is subjected to distillation. The boiling point of alcohol is about 20° lower than that of water, and consequently all the alcohol will be found in the first portion of the distillate. By several successive distillations the alcohol may be obtained nearly pure.

Exp. 139.—Pour off one half of the fermented liquor of Exp. 138, § 292, and reserve it for Exp. 143, § 298. With the remainder proceed as follows: Support the flask on the iron lamp stand, and, by means

of a delivery tube of No. 6 glass, connect it with a second flask capable of holding one third of the liquid, and placed on a water bath, as represented in Fig. 66.



Fig. 66.

From this second flask a delivery tube is carried to a small flask kept cool by immersion in cold water. Heat the liquid in the largest flask, so that it just boils: the vapor of alcohol, together with a certain amount of steam, passes into the second flask, which is kept just below the boiling point of water by being supported on the water bath in which the water barely boils. At this temperature a considerable portion of the alcohol, together with some water, passes over into the third flask, where it is condensed. Continue the operation until about one third of the liquid has passed out of the large flask. The liquid obtained in the third flask is a dilute alcohol; the odor of alcohol is distinctly perceptible, but the alcohol may not be strong enough to burn. In that case, support the third flask on the wire gauze over the lamp, and connect it by means of a delivery tube with another small flask, which is kept cool. Heat the contents of the flask gently until they just boil, and transfer the first teaspoonful of the liquid which condenses in the cooled flask to a porcelain dish. If the experiment has been successfully conducted, the alcohol thus obtained will be strong enough to take fire if a flame be brought in contact with it.

The alcohol obtained by successive distillations of a dilute alcoholic liquid still retains a certain amount of water. This water may be removed by adding quicklime, a substance which has a great attraction for water, and distilling the mixture. Alcohol perfectly anhydrous is called *absolute alcohol*. Exposed to the air, it attracts moisture. Ordinary strong alcohol contains about 10 per cent of water.

294. Exp. 139, § 293, affords an excellent example of what is known as *fractional distillation*. When the boiling points of several liquids differ by a considerable number of degrees, they may thus be separated from each other in a tolerable state of purity by observing the temperature of the boiling liquid, and collecting by themselves the succes-

sive portions of the distillate which come off within certain narrow limits of temperature. In operating with very volatile liquids, it is well to interpose a cooling apparatus between the retort, or *still*, and the receiver. Fig. 67 contains a representation of the so-called Liebig's condenser alluded to in § 34. It was first devised by Weigel.

A modification of the process of fractional distillation, known as *fractional condensation*, effects a more complete separation; for in this case the vapors, after leaving the retort, pass upwards through an inverted *worm*, which acts as a hot condenser; the temperature of the worm being so regulated that the less volatile bodies are almost entirely condensed, and so made to flow back into the retort (Fig. 68),

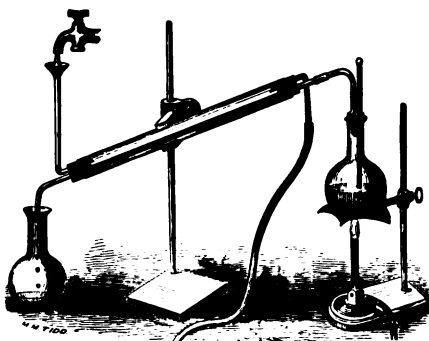


Fig. 67.

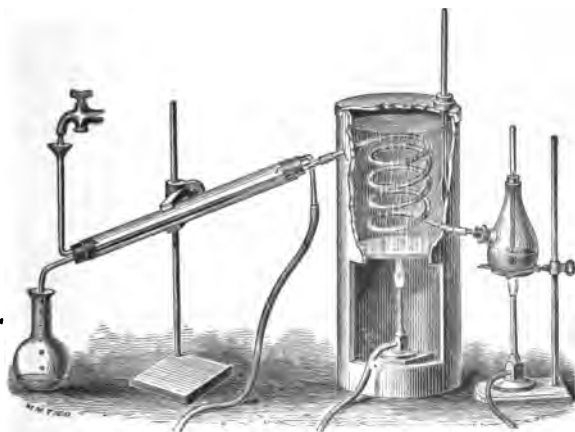


Fig. 68.

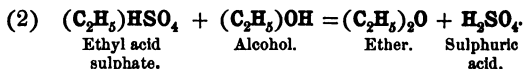
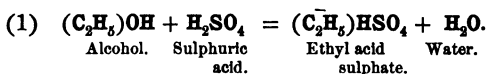
while the more volatile vapors go forward, and are condensed in the usual way in appropriate receivers.

295. Alcohol is much used in the arts. It forms the basis of all fermented and distilled liquors; it is employed as a convenient fuel; and formerly, when mixed with oil of turpentine, benzol, or other hydrocarbons, it was used for the production of light. It is extremely valuable as a solvent; for it dissolves many substances, such as resins and oils, which are insoluble in water. Thus shellac varnish is an alcoholic solution of a peculiar resin known as *shellac*; the *tinctures* of pharmacy are alcoholic solutions of medicinal principles.

In its chemical properties, alcohol acts as a weak base towards acids, and as a weak acid towards such basic elements as sodium and potassium. With these elements it reacts to form potassium ethylate ($\text{C}_2\text{H}_5\text{OK}$) and sodium ethylate ($\text{C}_2\text{H}_5\text{ONa}$), which are often spoken of as *alcoholic salts*.

296. **Ether.** — When a mixture of strong sulphuric acid and alcohol is heated in a retort, there distills over, together with water, a highly volatile, inflammable liquid known as *ether*. The distillate, which must be condensed in a well-cooled receiver, separates into two layers. The ether, being almost insoluble in the water, and lighter than it, forms the upper layer, and may be drawn off nearly free from water. The last portions of water are removed by allowing the ether to stand over quicklime, and then distilling.

The reaction between the sulphuric acid and alcohol may be represented as taking place in two stages: —



The alcohol and sulphuric acid are mixed in equivalent proportions; and, as the water and ether distill off, the loss is supplied by a stream of fresh alcohol flowing slowly, but without interruption, into the retort. The operation thus goes on continuously.

Exp. 140. — Into a small test tube put 10 drops of ordinary alcohol, and as much strong sulphuric acid, and heat the mixture gently over the lamp. Ether will be formed, and may be recognized by its peculiar odor.

The student should never attempt to perform any experiment requiring more than a very minute quantity of ether, since it is highly dangerous to work with this substance, on account of its great volatility and ready inflammability.

297. Ether is a colorless, very mobile, volatile liquid. It possesses a powerful odor, and, when inhaled, produces insensibility to pain: hence it is used in surgical operations. The vapor of ether is very heavy and exceedingly inflammable, and in certain proportions forms an explosive mixture with air.

Exp. 141. — Pour a small quantity of ether into the palm of the hand, and observe the rapidity with which it evaporates, and the sensation of cold which is caused by the evaporation.

Exp. 142. — Into a tumbler, or other very wide-mouthed vessel, put a few drops of ether. Cover the vessel loosely, and allow it to stand for a few moments; then bring a lighted match to the mouth of the vessel. The heavy vapor of ether will have displaced the air in the vessel, and will take fire at the mouth of the vessel with a sudden flash.

298. **Acetic Acid** ($C_2H_4O_2$). — When the alcoholic liquid formed by the fermentation of the juice of grapes, or apples, or other fruits, is exposed to the air, it gradually becomes sour, and is eventually converted into vinegar. Investigation shows that oxygen from the air has united with the alcohol, and changed it to *acetic acid*. Vinegar is a very dilute solution of acetic acid, containing about 2 to 4 per cent of the acid, together with coloring matter. In case it has been prepared from wine or from cider, it contains various impurities derived from the juice of the fruit.

Exp. 143. — Allow that portion of the alcoholic liquor of Exp. 138, § 292, which was not distilled, to remain for a number of days in a loosely covered vessel. The liquid will gradually become sour, and acquire the taste and smell of vinegar. The alcohol has been converted into acetic acid. Preserve this acid liquid for use in a subsequent experiment.

Vinegar, as has just been seen, may be produced by allowing an alcoholic liquid to become sour gradually, by exposure to the air in imperfectly closed vessels. On the large scale, however, it is generally made by allowing the air to have access to weak alcohol, spread in a very thin layer over a very great surface. The operation is conducted in large casks filled with wood shavings, over which diluted alcohol or

wine or wort is caused to trickle slowly. The cask is furnished with a false bottom, and with a false head perforated with small holes, which

serve to distribute the alcohol evenly over the shavings. Air enters the cask through holes, as at *a*, and escapes through the tubes *c c c*, and through several holes in the cover of the cask. The liquid which runs out of the cask may be returned to the top, until, after passing through the cask several times, the alcohol is entirely converted into acetic acid. The cask may be made of such size, and the flow so regulated, that the conversion of the alcohol to vinegar is complete after one operation. When prepared by the *quick process* above described, a small quantity of burnt sugar is added to the vinegar, to give it the dark color to which the public long ago became accustomed.

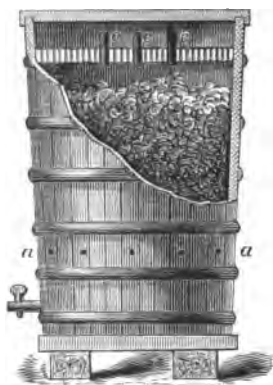


Fig. 69.

Just as the fungus known as *yeast* is needed in the preparation of alcohol from sugar (§ 291), so, for converting alcohol to vinegar by the method here described, the presence of another peculiar microscopic organism is essential. On first charging his casks with shavings, the vinegar manufacturer is at pains to soak them in vinegar taken from a cask which is already in working order and known to be charged with the fungus. When vinegar is made on the small scale, as in Exp. 143, the spores of the necessary fungus fall into the liquor from the air. In household economy it is customary to start a new vinegar cask by bringing to it, from an old cask, some of the matter called *mother of vinegar*, which is a sort of mucilaginous skin formed by the agglomeration of a multitude of the minute organisms known as the *acetic ferment* (*Mycoderma aceti*). The tiny, eel-like organisms often noticed in vinegar are the larvæ of a small fly often seen about apples and other fruits. They serve no useful purpose in vinegar making.

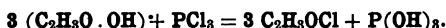
299. Acetic acid is one of the products of the destructive distillation of wood (§ 369). When thus obtained, it is known in the crude state as *pyroligneous acid*, which is a substance largely used in calico printing and for making acetates.

The pure acid is obtained by acting on some acetate, as sodium acetate, with sulphuric acid, and then distilling the mixture. At the ordinary temperature, acetic acid is a volatile

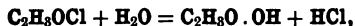
liquid possessing a pungent odor, but at 17° it becomes a transparent solid: hence the name *glacial acetic acid* applied to the strongest acid. It is a curious property of strong acetic acid, that it acts to dissolve or destroy abnormal growths of flesh (such as warts) without much action on the hair or upon non-delicate skin, as of the hand.

Exp. 144. — To the acid liquid of Exp. 143, § 298, or to 40 or 50 cc. of common vinegar, add powdered chalk (calcium carbonate) as long as the addition causes effervescence. Calcium acetate is formed, and remains dissolved in the liquid. Filter the solution, and evaporate the filtrate to dryness at a gentle heat. The solid residue is an impure calcium acetate. Place a portion of this calcium acetate in a small test tube, and heat it gently, together with a few drops of strong sulphuric acid. Acetic acid will be set free, and may be recognized by its peculiar odor. If ordinary vinegar be used in this experiment, it will be better to decolorize the solution of calcium acetate by mixing it with powdered boneblack before filtering (Exp. 109, § 241).

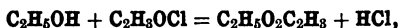
The *acetates* are important bodies, and many of them are used in the arts and in medicine. Aluminum acetate is used in dyeing (§ 573); lead acetate is familiar under the name of *sugar of lead*; an acetate of copper is known as *verdigris*; ethyl acetate is *acetic ether*. In one point of view, acetic acid may be regarded as the hydroxide of the hypothetical radical acetyl ($\text{C}_2\text{H}_3\text{O}$), which is capable of entering into many combinations, as if it were a metal. Thus there is an acetyl chloride ($\text{C}_2\text{H}_3\text{OCl}$), as well as acetyl hydroxide (acetic acid). Acetyl chloride may be prepared by treating acetic acid with phosphorus trichloride (PCl_3), the reaction being —



Acetyl chloride reacts with water, acetic acid and hydrochloric acid being formed according to the reaction —



the atoms of chlorine being replaced by hydroxyl. This reaction is frequently used in organic chemistry to detect the presence of the hydroxyl group. Thus, when ethyl alcohol is treated with acetyl chloride, the following reaction occurs:—

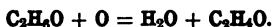


the product being hydrochloric acid and an ethereal salt known as ethyl acetate. In general, if on treating a substance with acetyl chloride we find hydrogen replaced by the acetyl group, we conclude that the substance contains the hydroxyl group.

Another way of regarding many of the organic acids is to admit that they contain the group carboxyl ($\text{CO} \cdot \text{OH}$) combined with a hydrocarbon group, which, in the case of acetic acid, is CH_3 . In accordance with this view, the formula of acetic acid would be written $\text{CH}_3 \cdot \text{CO} \cdot \text{OH}$,

or, graphically, $\text{CH}_3 - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$; and that of sodium acetate would be $\text{CH}_3 \cdot \text{CO} \cdot \text{ONa}$, or $\text{CH}_3 - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{ONa} \end{array}$.

300. Aldehyde ($\text{C}_2\text{H}_4\text{O}$).—When oxidizing agents are made to act on ethyl alcohol in a partial or limited way, the first result is the formation of a volatile liquid of pungent, suffocating odor, which has been called *aldehyde* (*alcohol dehydrogenatum*). It is produced by the removal of two atoms of hydrogen from the alcohol,—



By the further action of oxygen, aldehyde is readily converted into acetic acid,—



Aldehyde is a substance of considerable scientific interest, for it takes part in a great variety of familiar reactions. In vinegar making (§ 298), an abundant supply of air must be maintained; for, if air is lacking, much of the alcohol will be converted into aldehyde, which, owing to its extreme volatility, will escape as vapor, and thus be lost. Aldehyde is regarded as containing the group of atoms known as the *aldehyde group* (COH), and the symbol may be written as follows, to indicate this

view: $\text{CH}_3 \cdot \text{COH}$, or, graphically, $\text{CH}_3 - \text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$.

Aldehyde has a marked tendency to undergo polymerization. Among its polymers is a body known as *paraldehyde* ($\text{C}_2\text{H}_4\text{O}$)₃, which is a colorless liquid of suffocating odor, solidifying at 10° , and boiling at 124° . It is somewhat used in medicine as an anæsthetic and sedative, and for inducing sleep.

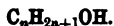
301. Chloral or Trichloraldehyde ($\text{C}_2\text{HCl}_3\text{O}$).—By replacing three atoms of hydrogen in the formula of aldehyde by as many atoms of chlorine, the formula of a body known as *chloral* is obtained. This compound is formed by passing chlorine through absolute alcohol. It is an oily fluid, which unites with a small quantity of water to form a crystalline hydrate, much used of late in medicine to induce sleep.

302. It is to be noticed that in studying ethyl alcohol, ether, aldehyde, and acetic acid, we have become acquainted with several members of the family of derivatives of the second hydrocarbon, ethane, of the list given in § 279. But in the same way we may

study the derivatives of either of the other hydrocarbons in that list, and become acquainted with alcohols, ethers, aldehydes, and acids, which correspond to those just mentioned, but which, while bearing strong resemblances to the ethane derivatives, do, nevertheless, differ from them in many particulars, and the more in proportion as their position in the series is more distant from that of ethane and its derivatives. Precisely as ordinary alcohol is a hydroxide of ethyl, so there are hydroxides of each of the radicals of the marsh-gas series (§ 279); thus, —

| | | | | Bolling Point. |
|-----------------------|---|----|-------------------------------------|----------------|
| Methyl alcohol is | $\text{CH}_3 \cdot \text{OH}$ | or | CH_4O , | 66.5° |
| Ethyl “ “ | $\text{C}_2\text{H}_5 \cdot \text{OH}$ | “ | $\text{C}_2\text{H}_6\text{O}$, | 78.4 |
| Propyl “ “ | $\text{C}_3\text{H}_7 \cdot \text{OH}$ | “ | $\text{C}_3\text{H}_8\text{O}$, | 97 |
| Butyl “ “ | $\text{C}_4\text{H}_9 \cdot \text{OH}$ | “ | $\text{C}_4\text{H}_{10}\text{O}$, | 116 |
| Amyl “ “ | $\text{C}_5\text{H}_{11} \cdot \text{OH}$ | “ | $\text{C}_5\text{H}_{12}\text{O}$, | 137 |
| Hexyl “ “ | $\text{C}_6\text{H}_{13} \cdot \text{OH}$ | “ | $\text{C}_6\text{H}_{14}\text{O}$, | 157 |
| Heptyl “ “ | $\text{C}_7\text{H}_{15} \cdot \text{OH}$ | “ | $\text{C}_7\text{H}_{16}\text{O}$, | 176 |
| Octyl “ “ | $\text{C}_8\text{H}_{17} \cdot \text{OH}$ | “ | $\text{C}_8\text{H}_{18}\text{O}$, | 195 |

which form an homologous series of alcohols of the general formula



303. Methyl alcohol (CH_3OH) resembles ordinary (ethyl) alcohol in being a light, colorless, inflammable liquid. It resembles alcohol also in its solvent powers, and is used in its stead for many purposes, such as dissolving shellac. It is prepared by the destructive distillation of wood (§ 369), and ordinarily contains certain impurities, which give to it an empyreumatic odor. It is commonly known as *wood spirit*, or *wood naphtha*. *Methylated spirit* is ordinary alcohol to which a certain amount of wood spirit has been added. This addition does not interfere with the use of the alcohol for many purposes to which it is applied in the arts, but renders it unfit for drinking.

304. Amyl alcohol ($\text{C}_5\text{H}_{11}\text{OH}$), or **fusel oil**, as it is usually called, is another primary alcohol (§ 305). It is a colorless liquid of disagreeable and characteristic odor, which will not mix with water, and is not readily inflammable. It is formed in the manufacture of brandy and whisky from potatoes and grain, and, as it has a boiling point much higher than that of ordinary alcohol, it may be separated therefrom tolerably

completely by the method of fractional distillation. Fusel oil burns with a somewhat smoky flame, and is sometimes used for purposes of illumination.

“**Amylene Hydrate**” ($(\text{CH}_3)_2 \cdot \text{C}_2\text{H}_5 \cdot \text{COH}$), or tertiary amyl alcohol (§ 305), is used in medicine to induce sleep.

305. Classes of Alcohols. — As will be seen from an examination of the structural symbols (§ 288) illustrating the possible isomerides of butyl hydroxide ($\text{C}_4\text{H}_9\text{OH}$), the hydroxyl group may replace hydrogen atoms which bear different relations to the rest of the molecule. Thus, in the formulas of normal butyl alcohol and of isobutyl alcohol, the hydrogen that is replaced by hydroxyl is in the methyl group, and the body may be regarded as containing the group — CH_2OH as a univalent radical. Alcohols having a structure such as this are known as *primary alcohols*. In the formula of the body called *secondary butyl alcohol* we have a substance represented as containing a bivalent radical, $=\text{CHOH}$; or, from another point of view, a body which may be regarded as methyl alcohol (§ 303), in which two atoms of hydrogen are replaced by marsh-gas radicals. Alcohols having this structure are known as *secondary alcohols*. Alcohols which are supposed to contain a trivalent radical, $\equiv\text{COH}$, as indicated in the formula of tertiary butyl alcohol (§ 288), and which may be considered to be derived from methyl alcohol by the replacement of three atoms of hydrogen by marsh-gas radicals, are called *tertiary alcohols*. These three classes of alcohols differ with respect to their oxidation products. On being oxidized, a primary alcohol gives first an aldehyde, and then an acid containing the same number of atoms of carbon as itself; a secondary alcohol yields first a ketone (§ 309), which, on further oxidation, splits up into acids containing smaller numbers of carbon atoms; whereas a tertiary alcohol breaks down at once on being oxidized, and there are formed acids or ketones which contain lower numbers of carbon atoms.

306. In the same way that ordinary ether ($(\text{C}_2\text{H}_5)_2\text{O}$) may be regarded as an oxide of the radical ethyl (C_2H_5), so the corresponding oxides of the other radicals of the marsh-gas series may be classed together under the general name of *ethers*: thus, —

| | |
|---------------------------------|--|
| Methyl oxide or Methyl ether is | $(\text{CH}_3)_2\text{O}$ or $\text{C}_2\text{H}_6\text{O}$ |
| Ethyl “ “ Ethyl “ “ | $(\text{C}_2\text{H}_5)_2\text{O}$ “ $\text{C}_4\text{H}_{10}\text{O}$ |
| Propyl “ “ Propyl “ “ | $(\text{C}_3\text{H}_7)_2\text{O}$ “ $\text{C}_6\text{H}_{14}\text{O}$ |
| Butyl “ “ Butyl “ “ | $(\text{C}_4\text{H}_9)_2\text{O}$ “ $\text{C}_8\text{H}_{18}\text{O}$ |
| Amyl “ “ Amyl “ “ | $(\text{C}_5\text{H}_{11})_2\text{O}$ “ $\text{C}_{10}\text{H}_{22}\text{O}$ |

When, as in the above series, we have the oxide of two similar radicals, it is known as a simple ether; but when two different radicals

exist in the oxide, the body is termed a *mixed ether*, as in the case

$\text{CH}_3 > \text{O}$ (ethyl methyl ether).
 C_2H_5

307. As the hydrocarbon radicals, methyl, ethyl, propyl, etc., unite with hydrogen to form *hydrides*, with oxygen to form *oxides* (ethers), and with hydrogen and oxygen to form *hydroxides* (alcohols), so they can form *salts* corresponding to the various acids. The formulas of these salts may be written by replacing the hydrogen of the acid by the different radicals. Thus ethyl sulphate is $(\text{C}_2\text{H}_5)_2\text{SO}_4$; ethyl nitrate is $(\text{C}_2\text{H}_5)\text{NO}_3$; methyl chloride is CH_3Cl ; and so on. In the case of an acid like H_2SO_4 , containing two replaceable atoms of hydrogen, there can be formed bodies like ethyl acid sulphate $((\text{C}_2\text{H}_5)\text{HSO}_4)$, corresponding precisely to potassium acid sulphate (KHSO_4) .

The salts of the marsh-gas radicals, *etheral salts* or esters, are often called *compound ethers*; methyl chloride is called *methyl hydrochloric ether*; ethyl sulphate is called *ethyl sulphuric ether*, or simply *sulphuric ether*. The term *sulphuric ether* is sometimes used to denote ordinary (ethyl) ether. This designation is, however, improper, as ordinary ether contains no sulphur whatever. Several of these compound ethers are manufactured in large quantities for the preparation of perfumery and flavoring extracts. Thus amyl acetate, or amyl acetic ether (made from fusel oil), has the odor and taste of the jargonelle pear; amyl valerianate has the smell and taste of apples, and is known as *apple oil*, ethyl butyrate has the flavor of pineapples, etc. The vapor of amyl nitrite $(\text{C}_5\text{H}_{11}\text{NO}_2)$, when inhaled, has a remarkable physiological influence on the beating of the heart. It has been found useful for relieving asthma and other spasmodic affections. A body known as *sulphonal*, an ethereal salt of a complex organic acid containing sulphur, occurs in colorless, tasteless crystals, much used for inducing sleep.

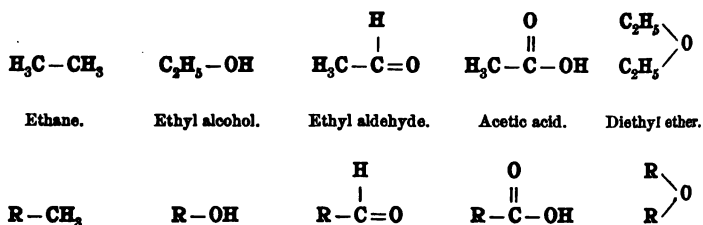
The preparation of one of these ethereal salts (ethyl acetate) may be illustrated by the following experiment:—

Exp. 145.—Into a small test tube put 10 drops of ordinary alcohol and the same amount of strong sulphuric acid. Add a crystal of sodium acetate as large as a small pea, and heat the mixture gently. Ethyl acetate will be formed, and may be recognized by its peculiar odor.

Corresponding to the oxygen compounds known as alcohols, aldehydes, and ethers, there are various sulphur compounds, notably the mercaptans or sulphur alcohols, such as $\text{C}_2\text{H}_5\text{SH}$ (ethyl mercaptan), and the sulphur ethers, as $(\text{C}_2\text{H}_5)_2\text{S}$, diethyl sulphide, etc., several of which occur in nature.

308. Each of the primary alcohols can be oxidized to its aldehyde, and finally to its acid: from amyl alcohol $(\text{C}_5\text{H}_{12}\text{O})$, for example, there is obtained valeric or valerianic aldehyde $(\text{C}_5\text{H}_{10}\text{O})$ and

valerianic acid ($C_5H_{10}O_2$). All these acids are monobasic, since they contain but one atom of hydrogen which can be replaced by a metal or other radical to form a salt. The relation of the several series of compounds to each other and to the hydroxide may be represented by the following graphic formulas, in which R stands for any marsh-gas radical:—

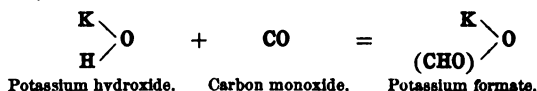


309. **Acetone** (C_3H_6O).—When an acetate is subjected to dry distillation, the substance known as *acetone*, a volatile liquid of characteristic odor, is obtained. It is also contained in small amount in the product of the destructive distillation of wood, and it may be prepared by oxidizing secondary propyl alcohol. It is an excellent solvent for resins, fats, etc. Acetone has been very carefully studied, and is believed to have the structure represented by the symbol $\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix} > CO$; i.e., it contains two methyl groups and carbonyl. It is a representative of an important class of similar compounds of marsh-gas radicals and carbonyl, isomeric with the aldehydes, but possessing very different properties, which are known collectively as *acetones*, or, more commonly, as *ketones*, for short. Acetone itself is often called *dimethyl ketone*. Ketones bear the same relation to secondary alcohols that aldehydes bear to primary alcohols. Each of them is produced by the partial oxidation of the corresponding alcohol. Ketones are readily transformed into secondary alcohols by the action of nascent hydrogen, just as aldehydes are changed to primary alcohols by this agent.

310. **Formic Acid** (CH_2O_2).—In the same way that acetic acid is a member of the ethane family, so is *formic acid* a derivative of the first hydrocarbon, methane, in the list of § 279. It is secreted by ants, and was first obtained by distill-

ing the bodies of these insects. It also occurs in the stinging nettle. It bears the same relation to methyl alcohol (CH_3O) that acetic acid does to ordinary (ethyl) alcohol, and may be prepared by the oxidation of methyl alcohol. Formic acid is interesting, because one of its salts, potassium formate, may readily be prepared from what are usually classed as inorganic substances.

If moist caustic potash be exposed to carbon monoxide at a temperature of 100° , the gas is slowly absorbed, and potassium formate is produced. From potassium formate thus made the acid itself may be obtained, —



Formic acid can best be prepared by heating oxalic acid with glycerin. Oxalic acid has the composition represented by the symbol $\text{C}_2\text{H}_2\text{O}_4$. When heated with glycerin, it is decomposed, and carbon dioxide and formic acid result, —



The formic acid distills over, and may be easily condensed. It is a colorless liquid, boiling at 100° , and having a peculiar penetrating odor.

Formic acid is one of a vast number of compounds which formerly were supposed to be produced only through the agency of living organisms, but which now can be made in the laboratory from inorganic substances. This synthetical construction of so-called organic substances has contributed to break down the distinction formerly drawn between organic and inorganic chemistry, until now there is hardly any vestige of it remaining.

311. One of the compounds of formic acid will serve as an excellent illustration of the value of *rational formulas* (§ 176). The formula of methyl formate ($\text{C}_2\text{H}_4\text{O}_2$) is the same as that of acetic acid, and it is evident that the *empirical formulas* can afford no means of distinguishing between these two substances. They may readily be distinguished, however, if methyl formate be written $\text{CHO} \begin{array}{l} \diagup \\ \text{O} \end{array}$, and acetic acid $\text{C}_2\text{H}_3\text{O} \begin{array}{l} \diagup \\ \text{O} \end{array}$; or if methyl formate be written $\text{CHO} \cdot \text{OCH}_3$, and

acetic acid $\text{CH}_3\text{CO} \cdot \text{OH}$: for these formulas represent to the eye and to the mind two distinct bodies.

312. **Formic aldehyde** (CH_2O) demands the students' attention, because of a supposition that it may perhaps be the first product formed in the leaves of plants when carbon dioxide from the air is decomposed there, as will be explained directly.

313. **The Fatty Acids.** — Starting from formic acid, which is the first acid in the list of which acetic acid is the second member, there is a most remarkable homologous series of acids, which is known as the *fatty-acid series*. Several members of this series are of very great industrial importance, and some of the best known of them are given in the following table. It will be observed, that while at the beginning of the list the substances are as thin as water, in which they dissolve freely, and that they exhibit unmistakable acidity, the solubility and the acidity become less and less marked as the proportion of carbon in the substances increases; and that the compounds, though still liquid at the ordinary temperature, become more and more oily. Finally, the higher members of the series are tasteless solids, though they melt readily to form oily liquids, and they exhibit only a weak acidity.

| Corresponding to | We have | | | Which occurs in |
|--|-------------|---|---|--|
| Methane (CH_4), | Formic | acid ($\text{HCO} \cdot \text{OH}$ | or CHO_2H), | Ants, pine needles, and stinging nettles. |
| Ethane (C_2H_6), | Acetic | " ($\text{CH}_3\text{CO} \cdot \text{OH}$ | " $\text{C}_2\text{H}_3\text{O}_2\text{H}$), | Vinegar. |
| Propane (C_3H_8), | Propionic | " ($\text{C}_2\text{H}_5\text{CO} \cdot \text{OH}$ | " $\text{C}_3\text{H}_5\text{O}_2\text{H}$), | Wood distillate. |
| Butane (C_4H_{10}), | Butyric | " ($\text{C}_3\text{H}_7\text{CO} \cdot \text{OH}$ | " $\text{C}_4\text{H}_7\text{O}_2\text{H}$), | Rotten ensilage, rancid butter. |
| Pentane (C_5H_{12}), | Valeric | " ($\text{C}_4\text{H}_9\text{CO} \cdot \text{OH}$ | " $\text{C}_5\text{H}_9\text{O}_2\text{H}$), | Valerian root and whale oil. |
| Hexane (C_6H_{14}), | Caproic | " ($\text{C}_5\text{H}_{11}\text{CO} \cdot \text{OH}$ | " $\text{C}_6\text{H}_{11}\text{O}_2\text{H}$), | Cocoonut oil. |
| Heptane (C_7H_{16}), | Cenanthylic | " ($\text{C}_6\text{H}_{13}\text{CO} \cdot \text{OH}$ | " $\text{C}_7\text{H}_{13}\text{O}_2\text{H}$), | Butter. |
| Octane (C_8H_{18}), | Caprylic | " ($\text{C}_7\text{H}_{15}\text{CO} \cdot \text{OH}$ | " $\text{C}_8\text{H}_{15}\text{O}_2\text{H}$), | Butter and cheese. |
| Nonane (C_9H_{20}), | Pelargonic | " ($\text{C}_8\text{H}_{17}\text{CO} \cdot \text{OH}$ | " $\text{C}_9\text{H}_{17}\text{O}_2\text{H}$), | Pelargonium plant. |
| Decane ($\text{C}_{10}\text{H}_{22}$), | Capric | " ($\text{C}_9\text{H}_{19}\text{CO} \cdot \text{OH}$ | " $\text{C}_{10}\text{H}_{19}\text{O}_2\text{H}$), | Limburger cheese. |
| etc. | | | | |
| | Palmitic | " ($\text{C}_{15}\text{H}_{31}\text{CO} \cdot \text{OH}$ | " $\text{C}_{16}\text{H}_{31}\text{O}_2\text{H}$), | Butter and tallow. |
| | Stearic | " ($\text{C}_{17}\text{H}_{33}\text{CO} \cdot \text{OH}$ | " $\text{C}_{18}\text{H}_{33}\text{O}_2\text{H}$), | Tallow and lard. |
| | Arachidic | " ($\text{C}_{19}\text{H}_{35}\text{CO} \cdot \text{OH}$ | " $\text{C}_{20}\text{H}_{35}\text{O}_2\text{H}$), | Peanut oil. |
| | Medullic | " ($\text{C}_{20}\text{H}_{41}\text{CO} \cdot \text{OH}$ | " $\text{C}_{21}\text{H}_{41}\text{O}_2\text{H}$), | Ox marrow and beef fat. |
| | Cerotic | " ($\text{C}_{26}\text{H}_{53}\text{CO} \cdot \text{OH}$ | " $\text{C}_{27}\text{H}_{53}\text{O}_2\text{H}$), | Beeswax. |
| | etc. | | | |

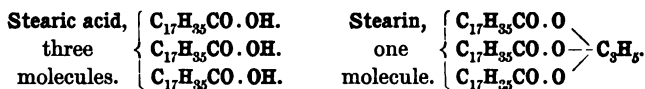
314. **Natural Fats and Oils.** — The various fats and nonvolatile oils obtained from both the animal and the vegetable king-

doms are in the main mixtures of three well-defined bodies, two of which, stearin and palmitin, are solid at the ordinary temperature, while the third, olein, is liquid.

Exp. 146. — Expose a test tube full of olive oil to cold by surrounding it with a mixture of salt and pounded ice. A portion of the oil solidifies, while another portion remains liquid. The solid portion is mainly palmitin; the liquid, olein.

Olive oil consists essentially of olein and palmitin; beef tallow is mainly stearin; lard is made up of olein and palmitin.

The chemical constitution of these bodies may be represented by the use of rational formulas. Stearin is a salt of stearic acid; and its formula may be derived from that of stearic acid by substituting, for three atoms of hydrogen in three molecules of the acid, one atom of the trivalent radical glyceryl (C_3H_5), thus: —



Stearin is glyceryl stearate; similarly palmitin is glyceryl palmitate, and olein is glyceryl oleate. Oleic acid does not belong to the same series with stearic and palmitic acids; but, from the association in nature of the oleates and the stearates, it is conveniently mentioned at this place. Butter consists mainly of salts of glyceryl related to the following acids: myristic, palmitic, stearic, caproic, caprylic, capric, and butyric, all members of the fatty-acid series.

315. In the manufacture of artificial butter, the clean fat of freshly killed beeves is subjected to processes of washing and slow cooling to remove the *animal heat*; it is then minced fine by means of a hashing machine, and *rendered* at a low temperature (ordinarily below $140^\circ F.$) by melting it by steam heat in jacketed kettles, from the tops of which the clear molten fat is drawn off, after some hours, while the membranous matter of the natural fat is allowed to settle at the bottom of the kettles. After all particles of membrane have been removed, the melted fat is allowed to cool somewhat, and is kept for several days at a temperature of 80° to $85^\circ F.$, in order that much of the stearin of the fat may crystallize. There is obtained in this way a semisolid mass, which is dipped off into bags of strong cloth, and subjected in a warm room to very heavy pressure, which squeezes out the still liquid *oleo oil*. This oil, at the temperature of the press room, is a clear, tasteless, amber-colored fluid containing olein and palmitin as well as some stearin; while a quantity of firm, hard, white stearin is left in the bags to be sold for other purposes than butter making. At

the ordinary temperature of the air, oleo oil is a light yellow, brittle solid, which crumbles like cheese when cut. Different grades of oleo oil are obtained, according as the fresh caul fat of the animal is operated upon at the slaughterhouse, or the harder suet which is cut off by the butcher when the meat is sold; but in both cases it is essential to success, that the animal fat shall be perfectly clean and sweet, and that the most scrupulous cleanliness shall be exercised in all the processes of manufacture.

The flavor of butter is imparted to the oleo oil by churning the latter with milk, or with milk and butter, at a temperature (about 80° F.) high enough to keep the materials in the melted state. The artificial butter thus obtained is called *oleomargarine*, and it is colored yellow (just as butter is usually colored) by means of annato (§ 434), and it is salted and worked much in the same way as in ordinary butter making.

In order to obtain the same consistency or *grain* that butter has, the mixture is cooled suddenly by running it from the churn into ice water, or upon pounded ice that is continually stirred; and to improve the consistency of the product, particularly in the winter, some soft fat, such as cotton-seed oil, or sesame oil, or lard, is often put into the churn with the oleomargarine and milk. At one time the term *butterine* was applied to oleomargarine with which a considerable proportion of cow's butter had been admixed; but at the present time the two terms appear to be used synonymously. Mixtures of beef fat and cotton-seed oil are sold nowadays under the name *cottolene*, as a substitute for lard in cooking. Oleo oil also is sometimes used as such for cooking purposes.

316. The various fats and oils are insoluble in water; they are, however, readily dissolved by certain liquids, such as ether, benzol, naphtha, oil of turpentine, etc.

Exp. 147. — Fill a small bottle half full of water, and pour in a few drops of olive oil. The oil remains on the top of the water, and is not dissolved by agitating the mixture.

Exp. 148. — Into a small bottle put two teaspoonfuls of concentrated ether, and add one quarter as much olive oil. Cork the bottle tightly, and shake it: the oil is readily dissolved by the ether.

317. **Manufacture of Soap.** — Very great industrial importance attaches to many of the natural fats and oils, on account of their use in the manufacture of soaps and stearin candles. In both of these industries, a hydroxide of glyceryl, *glycerin* ($\text{C}_3\text{H}_5(\text{OH})_3$), is obtained as a secondary product

The manufacture of soap may be illustrated by the following experiment:—

Exp. 149.—Dissolve 15 g. of solid caustic soda in 120 cc. of water. When the suspended impurities have settled to the bottom of the solution, pour off one half of the clear liquor into a deep iron or porcelain dish of at least 500 cc. capacity (Appendix, § 21); add an equal bulk of water and 50 g. of beef tallow. Bring the mixture to boiling, and boil it steadily for three quarters of an hour, supplying from time to time the water lost by evaporation; then add the remainder of the solution of caustic soda, and continue to boil steadily for an hour or more, allowing the liquid to become somewhat more concentrated towards the end of that time; then add 20 g. of fine salt, boil for a minute or two, and allow the liquid to cool. A part of the mass becomes solid, and rises to the top: it is hard soap.

The chemical action is thus explained: when tallow (glyceryl stearate and oleate) is boiled with sodium hydroxide, there is formed sodium stearate (and oleate) and glyceryl hydroxide. When common salt is added, the soap (sodium stearate and oleate), being insoluble in the saline liquid, separates as a solid. The liquid remaining contains in solution the excess of sodium hydroxide employed, as well as the salt and the glycerin.

Soap may be made more quickly by using castor oil instead of beef tallow. Mix 100 cc. of castor oil and 100 cc. of caustic-soda solution prepared as above, and boil for 30 minutes. Then add 150 cc. of water, bring to a boil, and add 20 g. of salt. The soap rises to the top, and may be removed when cold. Castor oil is mainly glyceryl ricinoleate. The chemical change is similar to that just described.

Exp. 150.—Heat some of the soap of Exp. 149 with soft water. A nearly clear solution will be obtained if the decomposition of the tallow or oil was complete. Add dilute hydrochloric acid until the solution is decidedly acid. The liquid will become turbid, and, on standing, will become covered with a layer of a fatty substance, which is a mixture of stearic and oleic acids (or mainly ricinoleic acid, if castor oil was used). The sodium chloride formed will be held in solution by the liquid.

Other bases beside caustic soda may be used to effect the decomposition of oils or fats into salts and glycerin. If caustic potash be used, a soft soap is formed; if slaked lime be employed, there is formed a lime soap, calcium stearate, etc., insoluble in water; if lead oxide be used, there results an insoluble lead soap formerly much used in medicine under the name of *lead plaster* or *diachylon*.

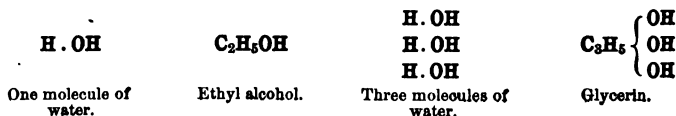
318. In Exp. 149, one of the products of the reaction, glycerin, remained dissolved in the solution of sodium chloride and hydroxide. This substance may be prepared as follows:—

Exp. 151.—Into a deep porcelain dish put 50 g. of litharge and 75 cc. water. Into this mixture stir 50 g. of olive oil, and boil the mixture steadily for 50 or 60 minutes, with constant stirring, and occasional addition of water to replace that lost by evaporation. The oil is gradually decomposed; an insoluble lead soap, such as is used for making yellow sticking plaster, is formed; and the color of the mass in the dish becomes lighter. When the oil seems to be entirely decomposed, pour off the liquid portion through a filter, add 50 cc. of water to the lead compound, boil for 5 minutes, and pass this liquid also through the filter. The glycerin is dissolved by the water, and with it passes through the filter. Evaporate the filtered liquid to dryness at a gentle heat: the glycerin will remain as a sirupy, non-volatile liquid, having a sweet taste. As the amount of glycerin obtained will be very small, it is well to transfer the solution, when nearly evaporated, to a watch glass, and to finish the evaporation on a water bath.

Glycerin, sometimes called **glycerol**, when pure, is a colorless, sweet-tasting, sirupy liquid, which mixes with water in all proportions. When heated in the air, it is slightly volatile; but it cannot be distilled in the air without decomposition, and the formation of vapors of acrolein, very irritating to the eyes,—



This same substance is formed when fat burns, and is the cause of the peculiar odor given off from the smoldering wick of a tallow candle. In an atmosphere of steam, however, glycerin distills without change, and the circumstance is availed of for preparing the pure article. Just as ethyl alcohol may be regarded as water in which an atom of hydrogen is replaced by the univalent radical C_2H_5 , so glycerin may be regarded as water in which the atoms of hydrogen of three molecules have been replaced by the trivalent radical glyceryl.

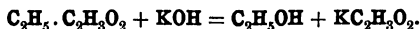


Glycerin is a valuable solvent, and it is employed also in medicine, mainly for external applications; its use depending upon the fact that it is but slightly volatile, and does not dry up or undergo change when exposed to the air.

319. **Nitroglycerin** is an oily liquid, heavier than water, which is formed when glycerin is allowed to flow gradually into a cool mixture of nitric acid and oil of vitriol. It is a highly explosive compound, being decomposed either by direct application of heat or by percussion. It is used for blasting purposes instead of gunpowder, but is very dangerous to transport. The danger in using it can be very much lessened by making the nitroglycerin immediately before use at the quarry or other locality where it is to be employed, or by impregnating with it some porous material. Dynamite, for instance, is infusorial earth thus impregnated.

The formula of nitroglycerin is $\text{C}_3\text{H}_5(\text{NO}_3)_3$, while that of glycerin is $\text{C}_3\text{H}_5(\text{OH})_3$; that is to say, three hydroxyl groups have given place to three groups of NO_3 . Or, from another point of view, the action has been the ordinary action of an acid on an hydroxide, the nitrate of the trivalent radical glyceryl has been formed, and nitroglycerin may be regarded as glyceryl nitrate. Nitroglycerin is the active constituent of a number of high explosives; it is also a valued medicament.

320. As has been stated, glycerin is a product of the manufacture of what are known as stearin candles. These candles are not, properly speaking, stearin, but are made of the solid fatty acids; namely, stearic and palmitic. Any process by which stearin (and, of course, palmitin and olein) is decomposed, so that the fatty acid or glycerin, or both bodies, are set free, is termed *saponification*, even in cases where no soap results from the reaction. The term *saponification* is used by chemists even more widely than in this case, for it is applied to the decomposition of any ethereal salt, resulting in the formation of an hydroxide of the hydrocarbon radical; for example, when ethyl acetate is heated with potassium hydroxide, ethyl hydroxide (alcohol) and potassium acetate result: thus, —

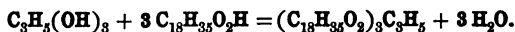


By treating a fat with sulphuric acid, it may be decomposed with formation of the fatty acids and glycerin, and the two

products can be readily separated from each other. The decomposition of fats may be effected also by the use of superheated steam; and in the manufacture of candles these two methods are employed to a very large extent, although the fatty acids are sometimes obtained by first forming a lime soap, and then decomposing it with acid, as the soda soap was decomposed in Exp. 150, § 317. The fatty acids are cooled and subjected to pressure, which separates the oleic acid: the solid acids are then molded into proper forms.

Candles are also manufactured from spermaceti, paraffin, and wax. Spermaceti is left as a waxlike solid when the oil of the sperm whale is chilled and subjected to strong pressure; when saponified, it yields palmitic acid and ethal ($C_{16}H_{34}O$). Paraffin is, at ordinary temperatures, a white solid having a pearly luster. It is probably a mixture of several hydrocarbons of the naphthene series (C_nH_{2n}) isomeric with the olefines (§ 335). The marsh-gas series of hydrocarbons is sometimes incorrectly termed the *paraffin series*, and its several members spoken of as if they were really *paraffins*. Paraffin occurs in petroleum, and, when the petroleum is distilled, it comes off in abundance at the latter part of the distillation. It is separated from the accompanying liquid hydrocarbons by chilling and pressing the mixture. It occurs also among the products of the distillation of bituminous coal and wood. Beeswax is mainly a salt of palmitic acid, melissyl palmitate, together with a free acid (cerotic acid). Chinese wax, produced by an insect belonging to the same genus as the cochineal insect, yields, on saponification, two bodies,—cerotin and cerotic acid. It is cerotyl cerotate.

321. **Artificial Fats.**—While by the various processes of saponification it is possible to obtain from the natural fats (with the elements of water) both glycerin and a fatty acid, it has also been found possible to reproduce the fats by bringing the fatty acids and glycerin together under appropriate conditions. In this case, water is eliminated precisely as water was set free in the formation of potassium nitrate by the reaction between potassium hydroxide and nitric acid (Exp. 37, § 68).



322. **Vegetable Oils.**—Of the oils and fats thus far considered, all, with two or three exceptions, have been of animal origin; all plants, however, contain some representative or representatives of this class. These vegetable fats and oils occur most abundantly in certain seeds and fruits, such as the

seeds of hemp, flax, cotton, sunflower, and the kernels of the stone of the peach; also in such nuts as the peanut, butternut, beechnut, almond, etc. Oil occurs also in grain, as may be illustrated by the following experiment:—

Exp. 152.—Dry two or three teaspoonfuls of corn meal on the water bath for an hour or two. Put the dry meal into a small bottle, and pour upon it twice its bulk of ether. Cork the bottle tightly, and shake it from time to time during half an hour. Finally filter the liquid into a clean porcelain dish (taking care that there is no lighted lamp or fire in the vicinity), and place the dish where there is a good draught. The ether will evaporate spontaneously, and a yellowish oil will remain.

All of these oils are called *fixed* oils: they leave a permanent greasy stain on paper, and cannot be distilled unchanged.

The fixed vegetable oils consist in great measure, like the animal fats, of stearin, olein, and palmitin; but many of them contain other substances in greater or less proportion. Thus bayberry tallow, a familiar example of a vegetable fat, consists in part of palmitin and palmitic acid, and in part of a substance known as *lauric acid* ($C_{11}H_{23}.CO.OH$).

323. Drying Oils.—Certain oils, especially linseed oil, when exposed to the air, gradually absorb oxygen and become solid. Such oils are called *drying oils*. This absorption of oxygen causes the evolution of a considerable degree of heat; in fact, cases of spontaneous combustion often occur from the taking fire of heaps of rags, tow, or other light material, saturated or smeared with oil.

324. Essential Oils.—To be distinguished from the non-volatile or *fixed* oils, are the volatile or *essential* oils. These compounds, in some points, resemble the fixed oils: they are inflammable, insoluble in water, and readily soluble in alcohol and ether; they are, however, more or less volatile at ordinary temperatures, and do not leave a permanent stain on paper. The essential oils are generally obtained by distilling with water the portion of the plant in which they occur. The essential oil is carried over with the steam, and separates from the water which is condensed in the receiver. Characteristic examples of essential oils are to be seen in oil of turpentine and oil of cloves, which are volatile liquids of well-known odor.

Exp. 153. — Into a glass retort of about 250 cc. capacity put 5 g. of whole cloves and 150 cc. of water. Insert the neck of the retort loosely into a receiver or flask, kept cool as directed in Exp. 9, § 33. Bring the water in the retort to boiling, and boil until one half of the liquid has distilled over. The water which condenses in the receiver will be rendered turbid by the oil of cloves, which has been carried over by the steam; and on standing, the oil, being heavier than water, will collect in drops in the bottom of the receiver.

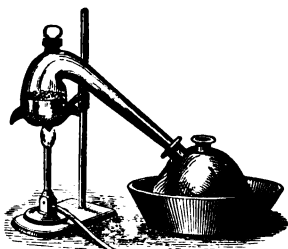


Fig. 70.

The oil possesses the characteristic odor of cloves, which it also communicates to the water with which it is in contact. The water may be poured off, and the volatility of the oil illustrated by dipping a piece of filter paper into it, and hanging the paper in the neighborhood of a gas flame.

The water, which, from its condensation with the oil of cloves, acquires the same odor, is an example of the fragrant distilled waters of the apothecaries.

325. Oil of Turpentine ($C_{10}H_{16}$). — When incisions are made in the trunks of certain species of pine, there exudes from the wounds a thick resinous substance known as *turpentine*. When ordinary turpentine is distilled with water, there comes over, mixed with the steam, the vapor of an oily liquid, which condenses in the receiver, and rises to the top of the condensed water. It is *oil of turpentine*. The residue in the retort is common rosin.

Exp. 154. — Into a glass retort of about 250 cc. capacity put 40 g. of crude turpentine and 200 cc. of water. Boil the liquid in the retort, and condense the vapor which is given off, as in Exp. 153, § 324. Drops of an oily liquid will rise to the top of the water in the receiver, and form a layer on its surface: it is oil of turpentine.

In this experiment the pitch of northern pines or of the spruce, etc., may be used instead of the crude turpentine.

Oil of turpentine is a thin, colorless, volatile liquid, and may be distilled unchanged. It will not mix with water, but dissolves freely in alcohol, wood spirit, ether, benzol, and naphtha, and in most of the essential oils. It is very inflammable, and burns with a smoky flame, as was shown in Exp. 104, § 237.

Exp. 155. — Into a small bottle half filled with water pour a teaspoonful of oil of turpentine, and shake the bottle. The liquid is rendered turbid by the drops of oil scattered through it; but these drops soon collect together, forming a layer on the top of the water.

Exp. 156. — Into a small bottle half filled with alcohol pour a teaspoonful of oil of turpentine, and shake the bottle. The oil of turpentine dissolves, and a clear homogeneous liquid results, which was formerly largely used in lamps as a burning fluid.

326. Oil of turpentine is chiefly valuable for its solvent powers. It dissolves the various resins, and is used in the preparation of varnish: it also dissolves sulphur and phosphorus with readiness, and is one of the best solvents of caoutchouc. Large quantities of it are used by painters also.

327. The essential oils find extensive application in perfumery, though they are sometimes replaced by substitutes artificially prepared. Thus for oil of bitter almonds is sometimes substituted nitrobenzol (§ 351); and, as has already been stated (§ 307), various ethereal salts, made from fusel oil and other alcohols, are prepared on a very large scale for the confectioner and perfumer.

328. Hydrocarbons isomeric with oil of turpentine are found in the other essential oils, such as the oils of bergamot, birch, cloves, caraway, lemons, etc.: most of them contain also distinctive compounds of carbon, hydrogen, and oxygen (§ 330). Certain of the essential oils contain sulphur: thus the essential oils of garlic, onions, and assafoetida contain $(C_3H_5)_2S$. This compound is the sulphide of the radical allyl (C_3H_5) . The pungency of the horse-radish is due to a sulphocyanide of the same radical.

It will be noticed that the radical allyl has the same formula as that assigned to glyceryl (§ 318). It is, however, merely isomeric with glyceryl, for the latter replaces three atoms of hydrogen, i.e., is trivalent, while allyl is univalent.

329. **Camphor** $(C_{10}H_{16}O)$. — Among the essential oils is classed ordinary camphor. It is obtained by distilling with water the wood of a variety of East Indian laurel. At ordinary temperatures, it is a white solid, which, like ice (§ 23), may volatilize or evaporate without first melting; on being heated to 175° , it melts readily, and boils at 204° , the vapor distilling unchanged. Camphor takes fire at a low temperature, and

burns with a very smoky flame: it is only slightly soluble in water, but dissolves readily in alcohol.

Exp. 157. — Into a tall, narrow beaker of about 50 cc. capacity put 2 or 3 g. of camphor. Roll up a piece of rather stiff paper so as to form a long conical cap which will fit into the top of the beaker. Place the beaker thus prepared in a sand bath, and heat it. The camphor soon melts and begins to boil, and the vapor of camphor is condensed on the upper part of the beaker and on the sides of the paper cone in delicate, snowlike crystals, or as a crystalline solid.

330. Camphor is a compound containing oxygen; and it is noticeable that many essential oils, when exposed to cold, deposit a certain quantity of solid matter analogous to camphor. These deposits are known generally as *camphors* or *stearoptenes*. **Menthol** ($C_{10}H_{20}O$) is a stearoptene somewhat resembling camphor in appearance, which occurs in the essential oil of mint. It is much used in medicine as an anæsthetic and disinfectant, and in the treatment of neuralgia and nasal affections. Other oxygenated essential oils are the oil of bitter almonds, oil of cinnamon, and oil of wintergreen. Some of these oils will be studied in the succeeding chapter.

331. **Cantharidin** ($C_{10}H_{12}O_4$), an irritating, poisonous substance, is the efficient agent of the Spanish flies used in medicine as a stimulant and for producing blisters. Several other bodies of analogous composition to cantharidin act as poisons, notably picrotoxin, which is obtained from the seeds of an East Indian fruit known as *Cocculus Indicus*.

The essential oils which have just been studied have no immediate relation to the marsh-gas series of hydrocarbons, which, with the derived compounds, has formed the main subject of this chapter. They are, however, conveniently studied in connection with the fats and fixed oils.

CHAPTER XVIII.

CARBON (continued).

332. Another homologous series of hydrocarbons is that whose general formula is C_nH_{2n} . The first member of this series is *olefiant gas* (C_2H_4). Members of this series are produced by the dehydration of alcohols, and some of them occur among the products of the distillation of various organic compounds.

333. **Olefiant gas, ethylene, or ethene** (C_2H_4), is a colorless gas, somewhat soluble in water. It may readily be prepared by the action of sulphuric acid on alcohol.

Exp. 158.—In a flask of at least 750 cc. capacity mix cautiously, with constant agitation, 120 cc. of oil of vitriol and 30 cc. of alcohol. Connect the flask, when cool, with a delivery tube dipping into the water pan, and apply a gentle heat. The colorless gas evolved from the mixture may be collected over water in the usual manner. The mass in the flask blackens, and towards the end of the operation froths considerably, so as to require constant watching. The gas burns with a white flame, as may be shown by applying a lighted match to the mouth of a bottle of the gas, and forcing the gas out by pouring water into the bottle.



Fig. 71.

The reaction which takes place consists in the removal of the elements of water from the alcohol:—



Other reactions, however, take place; and the gas prepared in this manner always carries with it some vapor of ether and undecomposed alcohol, together with the dioxides of carbon and of sulphur.

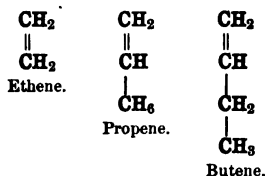
334. The name *olefiant gas* is derived from the fact, that, when it is brought into contact with chlorine, the two gases unite directly to form an oily liquid, *ethylene chloride* ($C_2H_4Cl_2$).

335. **Ethylene** is the first of a series of hydrocarbons known as *olefines*, each of which contains one atom less of hydrogen than the corresponding radicals of the marsh-gas series; thus,—

| | | | | | | | |
|---------------------|----|---------------|-------|--------|----|-------------|---|
| Ethylene (Ethene) | is | C_2H_4 , | while | Ethyl | is | C_2H_5 | . |
| Propylene (Propene) | " | C_3H_6 , | " | Propyl | " | C_3H_7 | |
| Butylene (Butene) | " | C_4H_8 , | " | Butyl | " | C_4H_9 | |
| Amylene (Pentene) | " | C_5H_{10} , | " | Amyl | " | C_5H_{11} | |
| etc. | | | | etc. | | | |

The members of this series act as bivalent radicals, being capable of combining with two univalent atoms to form saturated compounds.

They are also capable, under certain conditions, of forming substitution products. There is evidently some difference between the condition of the carbon atoms in the olefines and in the molecules of members of the marsh-gas series. What this difference is, is not known; but the condition by virtue of which the olefines act as bivalent radicals is usually represented graphically by two dashes between two carbon atoms in the structural formulas of members of the series; as —



This condition of carbon, in which the carbon atoms are related to each other in such manner that the molecule containing them can act as a bivalent radical, is called the *ethene condition*. The two dashes in the structural formulas mean nothing more than that the molecule of the body, represented as containing two carbon atoms in this relation, can, under proper conditions, combine with two univalent atoms.

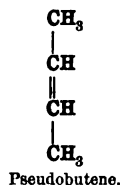
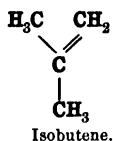
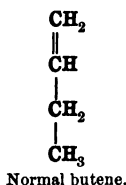
It is quite easy to pass from a member of the $\text{C}_n\text{H}_{2n+2}$, or marsh-gas series, to the corresponding member of the C_nH_{2n} , or ethene series: for example, if ethyl bromide ($\text{C}_2\text{H}_5\text{Br}$) be treated with an alcoholic solution of potassium hydroxide, the following reaction takes place: —



an atom of hydrogen and an atom of bromine being removed from the molecule of the ethane derivative, and an unsaturated molecule, ethene (C_2H_4), produced. This is a general reaction, applicable not only to the halogen substitution products of the hydrocarbons, but to other classes of derivatives as well. Conversely, ethene may be transformed into ethyl bromide by treating it with hydrobromic acid.

336. The olefines afford an excellent example of a series of polymeric (§ 287) bodies. They are all multiples of CH_2 , and all act as bivalent radicals; and two molecules of any lower member of the series may unite and condense to form one molecule of a higher member. Thus, for example, two molecules of propene (C_3H_6) can condense to one of hexene (C_6H_{12}). Another series of hydrocarbons, isomeric with the olefines, some members of which occur in petroleum, has been called the *naphthene series*. The naphthenes have been but little studied.

The olefines, beside forming isomers by way of polymerization, as well as in a manner similar to that illustrated by the members of the marsh-gas series, are capable of another form of metamerism, dependent upon the position, in the molecule, of the carbon atoms which are in the ethene condition; for example, we may have the following bodies, known as *butenes* or *butylenes*, represented by the structural formulas —

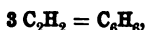


337. The members of the olefiant series afford an excellent illustration of the value to chemical theory of the determination of the vapor density of compound bodies, — a determination which is a purely physical operation. It will be seen that in each of these hydrocarbons there are two atoms of hydrogen for one atom of carbon, or two parts by weight of hydrogen for twelve parts of carbon. By analysis merely, the formula of these compounds could not be established. As an example, take butylene (C_4H_8). Analysis would only show that six parts by weight of carbon were combined with one part by weight of hydrogen; a determination of the vapor density would show the specific gravity of the gas referred to hydrogen to be about 28; and, as has been shown in § 168, the vapor density of a compound in a state of vapor is one half its molecular weight. If, then, 28 be multiplied by 2, the result will be 56 for the weight of the molecule; and the formula could not be C_2H_4 , or C_3H_6 , or anything, in short, except C_4H_8 . It is an important practical rule, *to obtain the true formula and the molecular weight of a volatile organic compound, multiply the vapor density by 2*. Another help in fixing the place of any member of a given series, if that member be a liquid at the ordinary temperature, is the determination of the boiling point; for it has been found that in these various series the boiling points of successive members increase in a nearly constant ratio.

338. **Glycols.** — The members of the olefiant series, acting as bivalent radicals, enter into a variety of compounds. One of these compounds, ethylene chloride ($\text{C}_2\text{H}_4\text{Cl}_2$), has already been mentioned (§ 334). Another, known as *ethylene glycol*, has the formula $\text{C}_2\text{H}_4 < \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$. It belongs to a group of bodies called *glycols*, which are related to the olefines in the same way that the alcohols, which con-

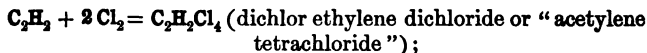
tain one hydroxyl group (§ 290), are related to members of the marsh-gas series. The glycols correspond to the hydroxides of bivalent metallic elements, such as calcium hydroxide ($\text{Ca}(\text{OH})_2$). These compounds are sometimes included in the general term *alcohol*, and are called *diatomic*, or *diacid*, or *dihydric* alcohols. In fact, the term *alcohol*, in its most extended sense, may be applied to any organic substance that can be regarded as derived from a hydrocarbon by the replacement of one or more atoms of hydrogen by hydroxyl. When three atoms of hydrogen are replaced, the alcohol is *trihydric*; thus glycerin ($\text{C}_3\text{H}_5(\text{OH})_3$), a compound already studied, may be regarded as a trihydric alcohol, and as derived from C_3H_8 (propane), three atoms of hydrogen being replaced by hydroxyl. The polyhydric alcohols, when oxidized, form acids, as ordinary alcohols do.

339. The Acetylene Series ($\text{C}_n\text{H}_{2n-2}$).—Acetylene (C_2H_2) is the first member of what is known as the *acetylene series*, the second member being allylene (C_3H_4), the third crotonylene (C_4H_6), the fourth valerylene (C_5H_8), and so on. The members of this series bear the same relation to acetylene or *ethine*, as it is sometimes called, that the higher members of the olefant series bear to ethene. Acetylene is interesting because it can be formed by the direct union of carbon and hydrogen at high temperatures, and because an enormous number of carbon compounds may be derived from it. When heated, the molecules of acetylene tend to *condense*, and to form other substances, one of which, benzene (C_6H_6), formed by the condensation of three molecules of acetylene,

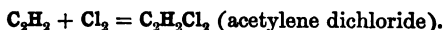


has very different properties from the members of the acetylene series, and is the simplest member of an exceedingly important homologous series, known as the *phenyl series*.

The members of the acetylene series all act as quadrivalent radicals. They can combine with four univalent atoms or radicals to form saturated molecules, or with two such atoms to form unsaturated molecules; for example, acetylene (C_2H_2) may combine with four atoms of chlorine,—



or with two atoms of chlorine,—



The condition of carbon which renders this result possible is called the *ethine* condition, and is represented graphically by three dashes between two carbon atoms: thus, —



This condition of carbon occurs but once in the molecules of the members of the series.

340. Acetylene (C_2H_2) is a transparent, colorless gas, which occurs in small quantities in illuminating gas. It may be formed by the direct union of carbon and hydrogen at very high temperatures. One way of obtaining it (and other unsaturated hydrocarbons) is to heat ethane and methane very hot. Another way is to treat bromoform (CHBr_3) with silver powder or with moist zinc copper. It is formed freely during the incomplete combustion of other hydrocarbons; and it has been discovered that the acetylene produced by the decomposition of other hydrocarbons, within the actual flame of burning coal gas, contributes largely to the illuminating effect of the flame. The peculiar odor noticed when the gas in a Bunsen lamp burns at the lower opening is due to the formation of acetylene. (See note, p. 394*b*.)

341. There are many other series of hydrocarbons, though only a few members of most of them are known. Lack of space prevents us from considering any more of these substances, excepting the so-called *phenyl series*, and a few individual members of one or two other series.

342. **The Phenyl, Benzene, or Aromatic Series ($\text{C}_n\text{H}_{2n-6}$).** — If the liquid and semiliquid products of the destructive distillation of bituminous coal, which collectively are known as *coal tar*, be subjected to redistillation, there will come off, first, a watery liquid, containing ammonium salts; next, a quantity (amounting to from 5 to 10 per cent of the tar employed) of oil lighter than water, and technically known as *light oil*, or, when purified, as *coal-tar naphtha*. After the “*naphtha*” comes the so-called *middle oil*, and then the *heavy oil*, which is followed by a grease called *anthracene oil*. The residue in the still is

known as *pitch*, or artificial asphaltum. It is used for covering roofs. When dissolved in naphthas, it forms a paint or varnish much used upon iron work.

The light oil mentioned above consists principally of a mixture of several hydrocarbons of the general formula C_nH_{2n-6} , known as the *phenyl series*. The members of this series, at present of most importance in the arts, are *benzol* (C_6H_6) and *toluol* (C_7H_8), otherwise called *benzene* and *toluene*. From these compounds are derived, by chemical processes, many of the beautiful and varied coloring matters known as *anilin dyes*. While coal tar is the chief industrial source of the hydrocarbons of the phenyl series, they have been obtained in less amount from other sources: petroleum from Rangoon, in the Kingdom of Burma, contains members of this series in small quantity.

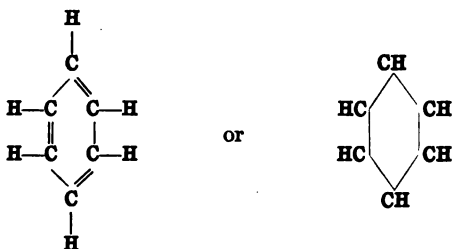
343. **Benzene, or benzol** (C_6H_6), at the ordinary temperature, is a mobile, colorless, volatile liquid, solidifying at 0° . Its vapor is very inflammable, and burns with a smoky flame. The illuminating power of ordinary coal gas is probably due in considerable measure to the vapor of benzol and its homologues. Benzol is valuable as a *solvent*, as it readily dissolves sulphur, phosphorus, caoutchouc, and other substances. Benzol also dissolves wax and fatty bodies, and may be used for removing grease spots from articles of silk and woolen.

344. Benzene (C_6H_6) may be regarded as the hydride of a radical (C_6H_5) called *phenyl*. Benzene would thus be called *phenyl hydride*, and the formula written $C_6H_5 \cdot H$. The synonymous names *benzene* and *benzol* are derived from the fact, that this substance can be obtained by the distillation, under proper conditions, of benzoic acid, — a substance which occurs in nature in gum benzoin.

345. The members of the phenyl series may all be regarded as derived from benzene by successive additions of CH_2 , and are formed by the replacement of one or more hydrogen atoms in benzene by hydrocarbon radicals.

346. In its chemical relations, benzene partakes of the properties of both the saturated and unsaturated hydrocarbons already considered. Thus, if subjected to the action of bromine, under ordinary conditions, monobrom benzene (C_6H_5Br) is formed. In direct sunlight, however, several unstable addition products may be obtained, the formula of the final term in the series being $C_6H_8Br_6$. Unlike the members of the marsh-gas series, an atom of carbon cannot be removed from the molecule of benzene, by oxidation or otherwise, without a

complete decomposition taking place. These facts indicate that benzene differs, in some way markedly, from the hydrocarbons of the series thus far considered; but they tell us nothing as to the cause of this difference. An examination of a few of the substitution products may give us some hints as to the matter. Innumerable attempts have been made to obtain isomeric substitution products of benzene, wherein one atom, or a single group of atoms, should take the place of an atom of hydrogen; but no such isomers have been obtained as yet: only one monobrom benzene ($\text{C}_6\text{H}_5\text{Br}$), one monochlor benzene ($\text{C}_6\text{H}_5\text{Cl}$), and one mononitro benzene ($\text{C}_6\text{H}_5\text{NO}_2$) exist, or, at least, none other has been obtained by any method used. Indeed, monobrom benzene has been prepared by replacing the six atoms of hydrogen in benzene *successively* by an atom of bromine: and it has been found that it is immaterial which hydrogen atom is replaced; the product is always the same. From these facts it is concluded that the hydrogen atoms, as in marsh gas, are of equal chemical value; that is, they bear one and the same relation to each other and to the rest of the molecule. This view finds expression in the structural formula generally adopted, as does also the fact that benzene is capable, under some conditions, of acting as an hexivalent radical:—



What the relation between the carbon atoms is, we do not know; and the double dashes of the first formula are to be regarded as merely indicating the hexivalent character of the molecule when it acts as an unsaturated body.

347. The homologues of benzene are formed by replacing the hydrogen by hydrocarbon radicals. Thus, the simplest of these homologues, toluene, or methyl benzene ($\text{C}_6\text{H}_5\cdot\text{CH}_3$), is closely analogous to benzene: it readily yields substitution products with chlorine, bromine, etc.; and this substitution may take place either in the methyl group (CH_3) or in the phenyl group (C_6H_5). If the replacement be in the methyl group, the prod-

ucts obtained bear a close resemblance in chemical properties to the derivatives of methane.

348. The number of aromatic hydrocarbons is very large, and amongst them a large number of isomerides occur. Thus we have the following isomeric hydrocarbons of the formula C_8H_{10} :—

$C_6H_4<\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}$, dimethyl benzene; $C_6H_5-C_2H_5$, ethyl benzene;

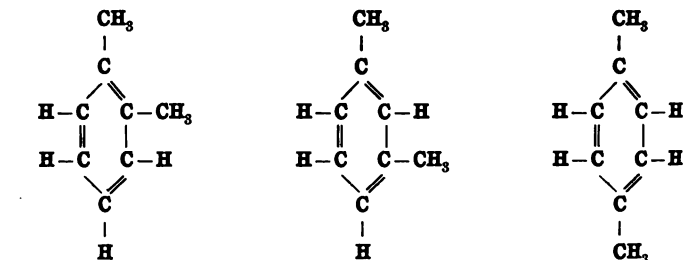
and, of the formula C_9H_{12} , the following:—

$C_6H_3<\begin{smallmatrix} CH_3 \\ CH_3 \\ CH_3 \end{smallmatrix}$, trimethyl benzene; $C_6H_4<\begin{smallmatrix} CH_3 \\ C_2H_5 \end{smallmatrix}$, ethyl methyl benzene;

$C_6H_5-C_3H_7$, propyl benzene; $C_6H_5-C<\begin{smallmatrix} CH_3 \\ CH_3 \end{smallmatrix}$, isopropyl benzene.
H

And yet these formulas, which represent a kind of isomerism, known as *isomerism of constitution*, due to a difference in the marsh-gas radicals, which have replaced hydrogen atoms, do not exhaust the possibilities; for isomerism in this series of hydrocarbons, and in their derivatives as well, may also be caused by a difference in the relative positions of the atoms of hydrogen which have been replaced by atoms or groups of atoms.

If in our structural formula of benzene we number the hydrogen atoms as in the accompanying diagram, it is evident that three isomeric disubstitution products, such as dimethyl benzene ($C_6H_4(CH_3)_2$), are theoretically possible, the methyl groups replacing the atoms of hydrogen in the following positions: 1 and 2, 1 and 3, 1 and 4, as indicated in the formulas:—



No further different relative positions of the two groups substituted for hydrogen are possible, for 1 and 5 bear the same relation to each

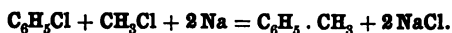
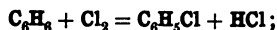
other as 1 and 3; 1 and 6, as 1 and 2. The fact that in the case of any disubstitution product of benzene only three *isomers of position* are known, is one evidence of the correctness of the view held as to the constitution of the benzene molecule.

349. The principal members of the phenyl series are given in the following table:—

| | |
|-----------------------------|-----------------------|
| Benzene or Benzol, | C_6H_6 |
| Toluene or Toluol, | C_7H_8 |
| Xylene or Xylol, | C_8H_{10} |
| Cumene or } Mesitylene } | or Cumol, C_9H_{12} |

Of the enormous number of derivatives of the aromatic series, we shall consider only a few of those which have special interest and importance. The great number of these bodies possible will be seen, if it is remembered that the replacement of hydrogen by other atoms or radicals may take place either in the phenyl group, or in the hydrocarbon radicals grafted upon this nucleus, forming the homologues and their several isomerides.

350. **Toluene**, or **toluol** (C_7H_8), resembles benzene in its chemical characters, and takes part in similar reactions. It may be formed from benzene by first introducing an atom of chlorine in place of an atom of hydrogen, and then replacing the atom of chlorine by methyl, in accordance with the following reactions:—



It may thus be regarded as methyl benzene ($C_6H_5 \cdot CH_3$); i.e., benzene in which one atom of hydrogen has been replaced by the radical methyl (CH_3).

351. **Nitrobenzene** or **Nitrobenzol** ($C_6H_5(NO_2)$). — By the action of nitric acid on benzene, an interesting compound, known as *nitrobenzene* or *nitrobenzol*, is produced.

Exp. 159. — Into a small flask put a teaspoonful of *fuming* nitric acid. Add a few drops of benzene, and warm the mixture *very gently* over the lamp. Chemical action takes place, and, upon subsequent dilution of the acid mixture with water, a heavy, oily liquid separates.

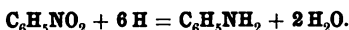
Nitrobenzene is a heavy, oily liquid, insoluble in water, but soluble in alcohol and ether. It has an odor resembling that of bitter almonds, and is somewhat used in perfumery under the name *artificial oil of bitter almonds*, or *essence of mirbane*.

Nitrobenzene is interesting as affording another example of a substitution compound in which the group of atoms NO_2 takes the place of hydrogen (compare nitroglycerin, § 319); it is, however, chiefly interesting from the fact that it is one step in the process of making anilin from benzol.

352. **Anilin** ($\text{C}_6\text{H}_5\text{NH}_2$) is a volatile, oily liquid, somewhat soluble in water, and readily dissolved by alcohol or ether. When pure, it is colorless, but on exposure to air it becomes of a reddish brown color. A characteristic reaction of anilin is afforded by its deportment to chloride of lime.

Exp. 160.—Stir up a teaspoonful of chloride of lime (bleaching powder) in five times its bulk of water, and filter the solution. Dissolve a drop of anilin in a teaspoonful of water, and add a few drops of this solution to a portion of the solution of bleaching powder. A beautiful purple coloration, turning to a dirty red, will form in the liquid.

353. Anilin may be obtained pure by distilling indigo with potassium hydroxide; it also occurs in very small quantity among the products of the distillation of coal, in the heavy oil of coal tar (§ 342); on a large scale, however, it is made from nitrobenzene by the action of reducing agents (§ 153), mainly by the reducing action of nascent hydrogen, obtained by treating iron with hydrochloric or acetic acid. The change which is effected may be represented by the following equation:—



The formation of anilin from nitrobenzene may be illustrated by the following experiment:—

Exp. 161.—Into a wide test tube put two drops of nitrobenzene and a few small fragments of zinc. Add half a teaspoonful of strong hydrochloric acid. Violent evolution of hydrogen takes place; and the nitrobenzene, which at first is visible in oily globules at the surface of the effervescing liquid, gradually disappears, being converted into anilin, which dissolves in the acid. More zinc or more acid may be added until this result is reached, but the zinc should be in excess. When the nitrobenzene has disappeared, and the action of the acid has ceased, dilute a portion of the liquid with an equal bulk of water, and

add a drop or two of the bleaching-powder solution used in Exp. 160, § 352. The characteristic purple color produced by the action of bleaching powder upon anilin appears in the liquid.

The formula of anilin is usually written $\text{C}_6\text{H}_5\text{NH}_2$; for its formation from nitrobenzene shows that it may be regarded as benzene in which one atom of hydrogen has been replaced by the radical (NH_2) , and be written $\text{C}_6\text{H}_5 \cdot \text{NH}_2$; or it may be regarded as ammonia (NH_3) in which one atom of hydrogen has been replaced by phenyl (C_6H_5) , and be

written $\text{N} \begin{smallmatrix} \text{H} \\ \text{H} \\ \text{C}_6\text{H}_5 \end{smallmatrix}$.

354. Anilin resembles ammonia in its behavior towards acids, uniting directly with them to form salts; thus with hydrochloric acid (HCl) it unites to form a compound $(\text{C}_6\text{H}_5\text{N} \cdot \text{HCl})$ or $\text{C}_6\text{H}_5\text{NH}_2\text{HCl}$ corresponding to ammonium chloride, and called *anilin hydrochloride* or *phenyl-ammonium chloride*.

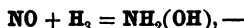
Exp. 162. — Pour a few drops of anilin into a porcelain dish, and hold over the dish a rod which has been dipped into strong hydrochloric acid. White fumes of anilin hydrochloride are produced. This experiment illustrates both the volatility and the basic character of anilin.

355. **Amines.** — Compounds that can be regarded as formed from ammonia by the replacement of one or more atoms of hydrogen by hydrocarbon radicals are called *amines*: thus

$\text{N} \begin{smallmatrix} \text{H}_2 \\ \text{C}_6\text{H}_5 \end{smallmatrix}$ (anilin) is *phenylamin*; $\text{N} \begin{smallmatrix} \text{H}_2 \\ \text{C}_2\text{H}_5 \end{smallmatrix}$ is ethylamin.

Trimethylamin $(\text{N}(\text{CH}_3)_3)$, obtainable from brine in which herring have been pickled, and from the waste liquors obtained in refining beet sugar, may be regarded as ammonia in which all the hydrogen has been replaced by the radical methyl. It is a volatile liquid, of rank, fishlike odor.

Hydroxylamin $(\text{NH}_2(\text{OH}))$ is interesting because it is ammonia in which one atom of hydrogen has been replaced by the group hydroxyl (OH) . It is a highly hygroscopic, white crystalline substance, which melts readily to a colorless, odorless liquid, rather heavier than water, which it somewhat resembles. When heated rapidly, it explodes. It combines with acids to form salts analogous to ammonium salts, and its aqueous solution has a strong alkaline reaction. Hydroxylamin can be prepared either by causing nascent hydrogen to combine with nitric oxide, —



or by the reduction of ammonium nitrite.

356. Toluidin.—From *toluene* may be prepared toluidin ($\text{C}_6\text{H}_5 \cdot \text{CH}_3 \cdot \text{NH}_2$) by precisely the same steps as are taken in the production of anilin from benzene.

357. Sometimes the term *amid* is applied as a general expression to all the substances in which one or more atoms of hydrogen in ammonia have been replaced by a radical, but it is applied also more definitely to those derivatives from ammonia which contain an *acid radical*. Thus in acetamid ($\text{C}_2\text{H}_5\text{O} \cdot \text{NH}_2$) one atom of hydrogen has been replaced by the hypothetical radical acetyl (§ 298), $\text{C}_2\text{H}_5\text{O}$, which is a component of acetic acid. Another familiar amid, called *asparagin*, is found in young shoots of plants, such as asparagus, peas, and beans: it is the amid of aspartic acid.

Acetanilid ($\text{C}_6\text{H}_5\text{ON}$ or $\text{C}_2\text{H}_5\text{O} \cdot \text{C}_6\text{H}_5 \cdot \text{NH}$) is much used as a sedative, and to allay fever and relieve pain. It is sometimes called *antifebrine*.

Chloral amid ($\text{CCl}_3\text{CH} \cdot \text{OH} \cdot \text{CONH}_2$) is an addition product obtained from chloral anhydride and formamid. It is an esteemed medicament for inducing sleep.

Phenacetin ($\text{C}_{10}\text{H}_{12}\text{NO}_2$) is used in medicine as a means of abating feverishness and neuralgic pains. **Piperazine** ($\text{C}_4\text{H}_{10}\text{N}_2$) is a synthetic compound, used as a medicament in the treatment of gout, rheumatism, etc. It has remarkable solvent power upon uric acid.

358. Anilin Colors.—Anilin itself, and the salts of anilin, are colorless when pure, but by exposure to the air they become more or less colored. By the action of various chemical agents on anilin, a great number of coloring matters may be obtained. Red, yellow, green, blue, and black, and that, too, in very great variety and beauty of shade, are thus, by difference in the chemical treatment, all obtained from the same raw material; namely, coal tar, a waste product which formerly was of very little value. The intensity of some of these coloring matters is very striking.

Exp. 163.—Take a crystal of *anilin red*, *fuchsine*, or *rubine*, no larger than the head of a pin, dissolve it in a small quantity of alcohol, and then dilute the solution in a clear bottle or in a white porcelain dish with a liter or more of water. The red tint communicated to this large quantity of water will be very perceptible.

359. In actual practice it is from a mixture of anilin and toluidin that the various so-called *anilin dyes* are prepared.

The chemical agents employed in the production of the anilin dyes are, in their general character, of an oxidizing nature. The effect of oxidation on the salts of anilin may be shown as follows:—

Immerse the poles of a galvanic battery in an aqueous solution of anilin acidulated with sulphuric acid. At the pole where oxygen is evolved, the solution becomes of a bright red color. In Exps. 160, 161, §§ 352, 353, the chloride of lime acted as an oxidizing agent, although the color there produced has little permanence.

The various coloring matters themselves are salts of several compound bodies which bear a certain resemblance to anilin, in that they possess a basic character, and that they of themselves are colorless. The beautiful and much-prized color known as *magenta*, sometimes called *fuchsine*, *rubine*, or *anilin red*, is the salt of a compound named *rosanilin*. This salt occurs in commerce finely crystallized. The crystals are of a brilliant green metallic color by reflected light, while by transmitted light they appear of an intensely red color. One of these coloring matters, known as *methylene blue*, has been recommended by physicians as a specific remedy for malaria and as an antiseptic. It has been used for treating rheumatism also.

Exp. 164.—In a dry test tube put a little dry mercuric chloride; add a few drops of commercial anilin. Heat the tube gently for a few moments, and dissolve the product in alcohol to which a little hydrochloric acid has been added. The deep magenta color of the solution is due to the presence of hydrochloride of rosanilin ($C_{20}H_{19}N_3 \cdot HCl$).

360. Phenol, Phenic, or Carbolic Acid (C_6H_5O).—Closely related to the phenyl series of hydrocarbons is a body known as *phenol*, *phenic*, or *carbolic acid*, which is obtained in abundance from coal tar. When pure, phenol crystallizes in colorless needles, sparingly soluble in water, which liquefy in moist air. It has an odor like wood smoke, and possesses powerful antiseptic properties. It is used, as are certain of its salts (*phenates* or *carbolates*), to prevent the spread of infectious diseases, and in the treatment of sores which give offensive discharges; it is also used in the preparation of a variety of disinfecting and purifying powders, of carbolic soap used for similar purposes, and as an insecticide. The *dead oil* of coal tar, which is used as a preservative of timber, owes its antiseptic properties, in some part, to carbolic acid, and also to a higher homologue of phenol called *cresol* or *cresylic acid*.

Carbolic acid possesses only weak acid properties. If its symbol be written $C_6H_5.OH$, it is seen to bear the same relation to the radical phenyl that the alcohols do to the radicals of the marsh-gas series. It is commonly called *phenol* by chemists, and is regarded as benzene in which one atom of hydrogen has been replaced by hydroxyl.

361. Phenol is one of a class of similar bodies called *phenols*, which are formed from benzene and its homologues by the replacement of one or more atoms of hydrogen in benzene by hydroxyl. As in the case of alcohols, there are phenols containing one, two, or three, etc., hydroxyl groups.

Resorcin ($C_6H_4(OH)_2$), called also **resorcinol**, or **metadiacid phenol**, occurs in colorless, odorless crystals. It is preferred in medicine to carbolic acid as an antiseptic, and as a remedy for fever, because it is non-irritant, and less poisonous than carbolic acid. Hydroquinone, an isomer of resorcinol, is used as a reducing agent in certain photographic processes.

The substance known as *pyrogallie acid* or *pyrogallol* is a triacid phenol of the composition $C_6H_3(OH)_3$.

Thymol ($C_{10}H_{14}O$), contained in oil of thyme, is a phenol of cumene ($C_{10}H_{14}$). It is a powerful disinfecting agent or germicide.

The phenols derived from toluene are known as *cresols* ($C_6H_4 < \begin{smallmatrix} CH_3 \\ OH \end{smallmatrix}$). *Cresols*, from wood tar, contains *cresols*.

362. The *dead oil* of coal tar contains several other acid bodies analogous to carbolic acid; it also contains small quantities of several different bases, among which is anilin (§ 353), and several hydrocarbons, also of no little interest, among which may be mentioned naphthalin (§ 365) and anthracene (§ 367).

A compound, known as *ichthyol* or *ammonium ichthyol sulphonate* ($C_{28}H_{36}S_3O_6(NH_4)_2$), prepared from the oil obtained by the destructive distillation of a bituminous mineral in the Tyrol, is remarkable for containing a considerable percentage of assimilable sulphur. It is very extensively used in medicine for the cure of skin diseases, rheumatism, etc.

363. **Trinitrophenol, Trinitrophenic, or Picric Acid.** — When phenic acid is treated with strong nitric acid, a compound known as *picric acid* is produced ($C_6H_3N_3O_7$). It is a bitter substance which forms yellow crystals not very soluble in water, but possessing great coloring power. It is soluble in alcohol and ether, and is used somewhat by dyers and brewers. Picric acid is formed by the action of nitric acid on various other organic compounds, especially on certain gum resins. It is manufactured from phenic or carbolic acid.

Exp. 165. — Into a flask of 150 cc. capacity put two teaspoonfuls of fuming nitric acid. Add cautiously, and very gradually, half a teaspoonful of crystallized carboic acid or of the liquefied crystals. The action which takes place is very violent, and nitrous fumes are copiously disengaged. When the action has subsided, allow the flask to become cold. Yellow crystals of picric acid will be found in the liquid.

This experiment should be performed where there is a good draught of air, and the flask should be kept at arm's length on each successive addition of carboic acid.

Exp. 166. — Dissolve 1 g. of crystallized picric acid in 125 cc. of water. Preserve one half the solution for use in a subsequent experiment; heat the remainder, and immerse in it a piece of white flannel, or a bit of white woolen yarn, which has been dipped in water and wrung out. Bring the liquid to a boil, remove the woolen material, and rinse it in water: it will be dyed a brilliant yellow.

Picric acid may be regarded as *trinitrophenol* (or *trinitrophenic acid*) ($\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$); i.e., phenol in which three atoms of hydrogen of the phenyl radical are replaced by NO_2 groups.

364. Picric acid is used in the preparation of potassium picrate, which is an ingredient of certain substitutes for gunpowder. The *picrates*, readily formed by the replacement of the hydrogen atom in the hydroxyl group, are yellow crystalline salts. When heated, they are decomposed with explosion. Picric acid itself explodes if heated suddenly, although with care it can be gradually sublimed. Potassium picrate will explode if struck with a hammer; and it, as well as ammonium picrate, has been used in the preparation of certain explosives.

365. **Naphthalin** (C_{10}H_8). — This hydrocarbon is an abundant product of the distillation of coal tar. It is a solid at ordinary temperatures, and separates in crystals when the hot so-called *middle oil* of tar is allowed to cool. These crude crystals are drained and pressed, then washed with sulphuric acid, and with alkali, if need be, and purified either by redistillation or by sublimation. Naphthalin is insoluble in water, but soluble in alcohol and the various naphthas. It forms white pearly scales, greasy to the touch, and has a characteristic unpleasant odor. It is not readily inflammable, but when lighted burns with a smoky flame. It is used in the manufacture of several coloring matters, and as a substitute for camphor for repelling moths from furs and woollens.

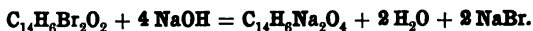
366. Naphthalin enters into direct combination with chlorine and bromine in different proportions. It also forms with these elements a great number of substitution compounds. As is the case with benzene, a variety of products are obtained by the substitution of groups of atoms for atoms of hydrogen in the naphthalin molecule.

Naphthol ($C_{10}H_7OH$) is a hydroxyl substitution product. Two varieties of this substance, known respectively as *alpha*- and *beta*-naphthol, are employed as powerful antiseptic agents. Beta-naphthol is much used in medicine as an intestinal antiseptic, and for treating skin diseases. Several naphthol products are valued dye stuffs.

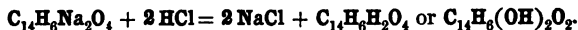
367. Anthracene ($C_{14}H_{10}$) is a white solid, obtained by subjecting to strong pressure the last pasty products of the distillation of coal tar. It is interesting because from it alizarin ($C_{14}H_8O_4$), a coloring matter formerly obtained from madder root (§ 433), is now made in large quantities.

The fact that alizarin, when heated with zinc dust, yields anthracene, led to the determination of the nature of alizarin and to its synthesis. From a study of the properties of alizarin it was found that the probable formula of the alizarin obtained from madder is $C_{14}H_6(OH)_2O_2$, that of anthracene being $C_{14}H_{10}$. An intermediate step in the synthetical process is the formation of a body known as *anthraquinone*, of which the formula is $C_{14}H_8O_2$. In order to form anthraquinone from anthracene, two atoms of hydrogen must be removed, and two atoms of oxygen introduced.

To accomplish this purpose, anthracene is dissolved in strong acetic acid; and chromic acid (§ 613), a powerful oxidizing agent, is added. The next step is to transform anthraquinone into alizarin by replacing two atoms of hydrogen in the molecule of anthraquinone by two hydroxyl groups. By treating it with bromine, dibrom anthraquinone ($C_{14}H_6Br_2O_2$) is formed; and, on heating this substance with sodium or potassium hydroxide, alizarate of sodium or potassium is obtained. The reaction with sodium hydroxide is as follows:—



Having thus produced alizarate of sodium, it is only necessary to add hydrochloric acid to obtain the alizarin. The reaction is expressed as follows:—



There are other methods of synthesis also, which may be employed on occasion.

368. Alizarin possesses in a remarkable degree the property of forming insoluble bodies with mordants (§ 574), and the

colors obtained in dyeing goods with it depend largely upon the character of the mordants which have previously been fixed upon the cloth. The alizarin colors are fast colors, not fading, as do the brilliant anilin dyes, when exposed to light or boiled with soap. The so-called *turkey-red* in cotton goods is a familiar example of an alizarin color.

369. Destructive Distillation of Wood.—In the distillation of wood, as in that of coal, the nature of the products varies somewhat according to the temperature employed. The gas obtained consists mainly of the oxides of carbon, marsh gas, and hydrogen. Of the liquid and semiliquid products, a portion is insoluble in water, and is composed of various hydrocarbons, some of which have already been studied. Of the portion soluble in water, the most important constituents are wood spirit (methyl alcohol, § 303), methyl acetate, acetone, and acetic or pyroligneous acid (§ 299).

The largest yield of acetic acid is obtained by distilling wood at low temperatures. The liquid portion, insoluble in water, contains, among other bodies, some of the homologues of benzol, and the body called *creosote*, which, when pure, is a colorless liquid of pungent taste and smoky odor. The peculiar odor of wood smoke is owing to the presence of this body. Creosote possesses very powerful antiseptic properties. Meat and fish may be preserved from putrefaction by immersion in a very dilute solution of creosote, or by exposure to wood smoke. Much of what is now sold as creosote is actually carbolic acid.

370. Oil of Bitter Almonds.—In § 327, among the essential oils was mentioned the *oil of bitter almonds*. This substance is closely allied with the phenyl series of hydrocarbons, and may be most conveniently studied at this point. If the kernels of the bitter almond be crushed, there is expressed a nearly colorless fixed oil, without taste or odor, and identical with that obtained from the sweet almond. If, however, the crushed kernels are moistened with water, fermentation occurs, and a volatile oil of peculiar aromatic odor is formed. Bitter almonds contain a peculiar nitrogenous substance, amygdalin ($\text{C}_{20}\text{H}_{27}\text{NO}_{11} \cdot 3\text{H}_2\text{O}$). Under the influence of another nitrogenous body contained in the kernels, and resembling somewhat the diastase of malt (§ 387), the amygdalin is converted into an

essential oil, the essence or oil of bitter almonds, of the formula C_7H_5O . There is formed at the same time a quantity of hydrocyanic acid (§ 270), which accompanies the essence when it is distilled, and communicates to it its highly poisonous qualities. The purified oil is not poisonous.

371. The formula of the oil of bitter almonds is C_7H_5O , and it may be regarded as a hydride of a hypothetical radical, benzoyl (C_7H_5O). The relation of the oil of bitter almonds to the phenyl series (§ 342) is seen by regarding it as an aldehyde, called *benzoic aldehyde*, bearing the same relation to toluene, C_7H_8 (§ 350), that ordinary aldehyde (§ 300) does to ethane (C_2H_6). It behaves like an aldehyde. In contact with the air, it oxidizes to benzoic acid ($C_7H_5O_2$), which, to carry out the same comparison, answers to acetic acid; and by the action of nascent hydrogen it is converted into a compound which corresponds to alcohol, benzyl alcohol (C_7H_9O).

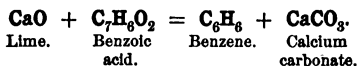
The relations of these compounds to each other are shown in the following table:—

| | | | | |
|--------------------|-----------------|-----------------|---------------------------|---------------------|
| <i>Hydrocarbon</i> | Ethane | C_2H_6 | Toluene or methyl benzene | C_7H_8 . CH_3 |
| <i>Radical</i> | Ethyl | C_2H_5 | Benzyl | C_7H_5 . CH_2 |
| <i>Alcohol</i> | Ethyl alcohol | C_2H_5 . OH | Benzyl alcohol | C_7H_5 . CH_2OH |
| <i>Aldehyde</i> | Acetic aldehyde | CH_3 . COH | Benzoic aldehyde | C_7H_5 . COH |
| <i>Acid</i> | Acetic acid | CH_3 . $COOH$ | Benzoic acid | C_7H_5 . $COOH$ |

372. The *true alcohols* of the phenyl series are formed from the homologues of benzene by a substitution of hydroxyl for an atom of hydrogen in a marsh-gas radical existing in them; and these alcohols are, like the marsh-gas alcohols, capable of oxidation to aldehydes, acids, etc.

373. **Benzoic acid** ($C_7H_5O_2$) occurs in many balsams, being found most abundantly in "gum benzoin," which is a vegetable exudation that contains several resins as well as benzoic acid. It may be prepared artificially from bitter almonds, as has been stated. It may also be prepared by oxidizing naphthalin with nitric acid, and heating the product with slaked lime. Calcium benzoate is thus produced, from which benzoic acid may be set free. Benzoic acid is a white crystalline solid, of pearly luster.

If benzoic acid is distilled with excess of lime, benzene is produced in accordance with the equation—



Salicylic acid ($C_7H_5O_3$) or **hydroxybenzoic acid** (C_6H_4 . OH . $COOH$), which may be regarded as phenol in which one atom of hydro-

gen of the phenyl radical has been replaced by carboxyl, occurs in the form of methyl salicylate in oil of wintergreen. Salicylic acid is largely used as a medicament in acute rheumatism: it is an excellent antiseptic, and several of the salicylates as well have been largely used in antiseptic preparations.

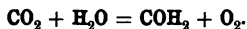
Salol ($\text{C}_6\text{H}_4\text{OHCOO} \cdot \text{C}_6\text{H}_5$), or **phenol salicylate**, is a white, crystalline, nearly tasteless powder of a faint aromatic odor. It is much used in medicine as an antiseptic, both internally and for the treatment of wounds.

CHAPTER XIX.

CARBON (continued).

374. In this chapter several of the natural organic compounds will be considered which play a part in the life and growth of plants and animals, or are the direct product of such growth. A great number of different compounds occur in the vegetable kingdom, some being found only in particular species of plants, or even being confined to single portions of particular plants, while others occur almost universally in nearly all vegetable organisms. Among these substances which occur so widely diffused are *water*, which sometimes amounts to 90 per cent of the green plant, *woody fiber* or *cellulose*, *gum*, *starch*, and *sugars*.

These substances are all derived from the carbon dioxide which exists in very small proportion in atmospheric air. The leaves of plants contain a substance called *chlorophyl* ("leaf green"), which has the power, under the influence of sunlight, to split up carbon dioxide in such manner that the carbon is retained in the plant, while the oxygen escapes into the air. It has been thought by several chemists that carbon dioxide and water are decomposed simultaneously by the chlorophyl grains in accordance with the equation —



But COH_2 is the formula of a well-known substance named *formic aldehyde* (§ 312), and, on multiplying COH_2 by 6, we obtain the formula of grape sugar ($\text{C}_6\text{H}_{12}\text{O}_6$); and it is easy to conceive that other sugars, as well as starch and cellulose, might be formed by subtracting one or

more molecules of water from grape sugar. However this may be, it is easy to see with the microscope that starch is actually formed in green leaves, as one result of the decomposition of carbon dioxide; and it is certain that this act of decomposition is the starting point of all forms of life, for plants get their food directly in this way, or by feeding on other plants, while animals, in their turn, feed either upon plants or on other animals.

The class of bodies known as *sugars* contains many varieties, of which the most familiar is ordinary *cane sugar*.

375. Cane sugar, or sucrose ($C_{12}H_{22}O_{11}$), occurs in the juice of various plants, notably in that of the sugar cane, sorghum, Indian corn, beet root, sugar maple, and certain varieties of palm. In this country, sugar made from the cane is used almost exclusively, but on the continent of Europe large quantities of this kind of sugar are made from the beet root. It is obtained from one or another of these sources in different countries, according to local conditions, and more especially according to the character of the tariffs or excise laws which are enforced. Naturally it can be prepared most cheaply from the sugar cane, but several European governments have established systems of bounties which have enabled their citizens to make sugar from beet roots, and this system has been recently introduced into several American States.

376. Sugar Manufacture.—In the manufacture of cane sugar, the juice is extracted from the canes by pressing them between strong iron cylinders. The liquid thus extracted contains not only sugar in solution, but also certain albuminous and waxy matters, and has a great tendency to ferment. It is therefore immediately treated with a small proportion of milk of lime, and heated for a short time. The lime serves to correct any acidity, and at the same time enters into combination with some of the impurities of the juice; the albuminous matters, coagulated by the heat, entangle these impurities, and rise with them as a thick scum to the surface of the liquid. The scum is removed, and the clear liquid is evaporated in open pans until of such a consistency, that crystals of sugar will separate from the sirup when it is allowed to cool. The crystals, after draining, form what is known as *brown sugar*; the mother liquor which drains off is molasses.

Until recently almost all the sugar manufactured was exported from the place of its production as *brown* or *muscovado* sugar, and was subsequently refined elsewhere. The *refining* consists in dissolving

the sugar in water, removing the impurities and coloring matters by filtering the liquor, and passing it through layers of bone charcoal, and then evaporating and crystallizing. The evaporation is conducted in a peculiar manner. If a solution containing a certain amount of common salt, or of almost any other inorganic substance, be evaporated, the salt is recovered unchanged, no matter how rapidly or how slowly the evaporation takes place: this is not the case with sugar. If a solution of cane sugar be boiled, a certain amount of the sugar undergoes a change: it is converted into another variety of sugar, or rather a mixture of two varieties of sugar. These varieties of sugar (which will be considered hereafter) do not crystallize out with the cane sugar, but form the main part of the molasses which drains off from the crystals. The amount of sugar which is thus changed depends, among other things, upon the length of time during which the solution is boiled, and also upon the temperature employed. By boiling in open pans, much sugar would thus be lost; and the sirup would become discolored, since some of it would be overheated where it clings to the pan. Hence in sugar refineries the sirup is boiled down in enormous, closed, iron or copper kettles, from which the air can be exhausted. Under these circumstances the solution boils at a much lower temperature than it would in the open air, and the risks of changing and of burning the sugar are avoided. When a sufficient degree of concentration is reached, the liquor is removed from the *vacuum pan*, as the kettle is called, and allowed to crystallize. The crystals are dried, either by allowing them to drain in molds (loaf sugar), or by forcing the mother liquor out by means of a centrifugal machine (granulated sugar). When, by further concentration of the liquor which drains off, and by repeated crystallizations, the greater part of the sugar has been obtained, the mother liquor remaining from the last crop of crystals is sold as *sirup*. Until within a few years, almost all the refining of sugar was done in Europe and the northern United States, and enormous quantities of sugar are still refined in these countries; of late years, however, vacuum pans and other improved apparatus have been introduced into the places where sugar is produced, and very good white sugar is there made directly from the juice of the cane. The following experiment will illustrate the principle of the vacuum pan alluded to above:—

Exp. 167.—Fill a round-bottomed flask of 500 cc. capacity half full of water, and boil it over the lamp. When the boiling has continued for some time, and the air in the upper part of the flask has been expelled by the steam, remove the lamp, grasp the neck of the flask with a dry warm towel, and immediately insert a tightly fitting cork. Support the flask in an inverted position, and pour cold water over the bottom, which is now uppermost, so as to condense the steam: there will be formed a vacuum above the water, and boiling

will recommence. This may be repeated several times, until the water has cooled down to a considerable extent.

377. The process of obtaining sugar from the beet root differs somewhat from that above described, because the cells of the soft and pulpy beet root, unlike those of the hard cane, do not need to be crushed or broken, and because the beet root contains a larger number of objectionable constituents than the cane does. By cutting the roots into slices and exposing these chips to a current of warm water, the sugar of the beet *diffuses* into the water; and there is obtained a comparatively pure solution, which is subjected to treatment analogous to that applied to cane juice. In some parts of the United States comparatively small quantities of sugar, and more especially of sirup, are made from sorghum and from the sap of the sugar maple; and in the East Indies considerable quantities are made from the juice of several varieties of palm, especially the date palm.

The crystallized sugar obtained from all these sources is identical with that obtained from the sugar cane. Care is, however, required in the purification, in order to remove completely a peculiar taste which betrays the origin of the sugar. Maple sugar and palm sugar are sold in the crude state, the peculiar taste being agreeable to many persons; beet sugar is always refined, as the taste of the crude article is offensive to every one.

Exp. 168. — Stop the neck of a funnel loosely with a bit of pumice stone, and fill it nearly to the top with common maple sugar which has been reduced to a rather fine powder. Prepare a saturated solution of sugar by dissolving 50 g. of white sugar in 20 cc. of hot water, and allowing the solution to cool. Pour some of this solution upon the maple sugar as it lies in the funnel, so as to make a layer 0.5 cm. thick. Support the funnel in a small bottle, cover it with a sheet of paper, and let it remain for some time. The solution will gradually work its way through the maple sugar; and, being already saturated, it will not dissolve any of the sucrose, but it will dissolve and carry away considerable quantities of coloring and flavoring matters, so that, when the maple sugar has drained, it will be much lighter colored than before, and will have lost, to a certain degree, its peculiar taste.

378. Sucrose is readily soluble in water, and may be obtained in large transparent crystals. Rock candy is nothing more than crystals of pure cane sugar. Sucrose melts at 160° to a colorless liquid, which, on cooling, forms a transparent

amber-colored mass, *barley sugar*. When sucrose is heated to 215° , water is given off, and a brown mass, *caramel*, remains.

Exp. 169.—Heat *cautiously* a small quantity of white sugar in a porcelain dish until it melts. Allow the pasty liquid to cool rapidly: the product is *barley sugar*. Heat again to a still higher, but not too high temperature: the sugar turns brown, froths, gives off pungent vapors, and there remains a dark brown mass, which is *caramel*. This substance is soluble in water, and is used to color soups, ale, brandy, cider, wines, vinegar, and so forth. If sugar be heated rapidly and rather strongly, it will take fire and burn, leaving a black carbonaceous residue.

379. **Lactose**, or **milk sugar** ($C_{12}H_{24}O_{12}$), is an animal product nearly related to cane sugar. It is less sweet and less soluble in water than cane sugar. It occurs in the milk of the mammalia, and is obtained, chiefly in Switzerland, by evaporating the whey of cow's milk. It crystallizes in hard, gritty crystals, which contain one molecule of water of crystallization.

380. Another sugar closely allied to cane sugar is **maltose** ($C_{12}H_{22}O_{11} \cdot H_2O$). It is found in sprouted grain and seeds, and may be prepared by acting upon starch with saliva. Some of it is produced also when starch is acted upon by hot dilute acids. It forms agglomerations of minute needlelike crystals of not very strong sweetish taste.

381. **Dextrose**, or **grape sugar**, called also **glucose** and **starch sugar** ($C_6H_{12}O_6$), occurs, together with cane sugar, in sorghum stalks and in many fruits. It is a constituent of molasses, and is often to be seen incrusting old candied raisins. Granules of it are apt to form in honey which has been kept for a long time. Enormous quantities are prepared artificially from starch by boiling it with dilute sulphuric acid. Maize starch serves for this purpose in America, but in Germany potato starch is used.

Exp. 170.—Into a flask of 250 cc. capacity introduce 100 cc. of water. Add 1 cc. of strong sulphuric acid, and heat the mixture to boiling. In a porcelain mortar, rub 10 g. of starch with enough water to make a cream, and pour the mixture little by little into the boiling liquid, taking care not to interrupt the boiling. The starch dissolves without forming a paste. Boil for three or four hours, replacing from time to time the water lost by evaporation, and then add powdered chalk (calcium carbonate) until the liquid is no longer acid.

When the mixture has become cold, filter off the insoluble calcium sulphate formed by the action of the sulphuric acid on the calcium carbonate, and evaporate the solution at a gentle heat to a sirupy consistency. The solution contains dextrose, which, on long standing, may separate from the liquid in minute crystals; but it is to be noted that dextrose crystallizes or granulates far less readily than sucrose does.

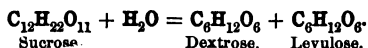
Dextrose may be obtained from cellulose also, i.e., from woody fiber (§ 396), by treating linen or cotton or paper shreds, or even sawdust, with strong sulphuric acid. The mixture is allowed to stand for 24 hours, and is then diluted with a large quantity of water, and boiled. The acid is subsequently neutralized with chalk, and the dextrose obtained, as in Exp. 170.

It is to be remarked that dextrin (§ 391) and some maltose (§ 380) also are formed at first, when starch is heated with dilute acids; but finally, after longer action of the hot acid, dextrose remains as the sole product. Practically the starch sugars of commerce often contain all three of the above-mentioned substances. Nowadays the term *glucose* is often restricted to liquid, sirupy products which contain much dextrin as well as dextrose, while those solid products which consist largely of dextrose are called *grape sugar*.

382. Dextrose as obtained from starch is used in the manufacture of alcohol (§ 292) and for strengthening and sweetening certain varieties of beer and wine, as well as for making sirups and confectionery. It possesses less sweetening power than cane sugar, and the introduction of it into articles ordinarily made from cane sugar is sometimes to be regarded as a kind of adulteration.

383. Fruit sugar, fructose, or levulose ($C_6H_{12}O_6$), is closely related to grape sugar, and occurs mixed with it in honey and molasses and in many kinds of fruits. It is formed, together with dextrose, when solutions of cane sugar are boiled for a long time, and especially when the hot solutions are slightly acid. This fact is one of great importance in its bearing on the manufacture of sugar. As has been explained in § 376, very considerable amounts of cane sugar are lost even in the best-conducted processes of boiling down saccharine juices.

By the action of yeast,—that is to say, of a substance called *invertin*, which is contained in yeast,—cane sugar may be split into dextrose and levulose, in accordance with the equation—



Chemical reactions in which, as in this case, compounds are broken up and resolved into other compounds by taking on the elements of water, are spoken of as processes of *hydrolysis* ("a dissolving"). Levulose may also be made directly from inulin (§ 390) — a substance which is found in the roots of the dahlia and some other plants — by boiling it with dilute acids, in the same way that glucose is made from starch (Exp. 170, § 381). Fruit sugar does not crystallize or granulate, but is left as an amorphous mass when its solution is evaporated.

384. The most striking physical property of the sugars is their action upon polarized light. If a beam of polarized light be passed through a solution of cane sugar, the plane of polarization will be rotated towards the right: the same is true of glucose, though in a less degree, and hence the name *dextrose* (from the Latin *dextra*, "the right hand"). Levulose, on the contrary, turns the plane of polarization to the left (Latin, *laeva*, "the left hand"). The amount of rotation in any case depends upon the amount of sugar in the solution examined, and upon this fact methods have been based for the quantitative estimation of cane sugar in sirups or solutions thereof.

A familiar test for dextrose, levulose, and lactose, is afforded by their chemical action on an alkaline solution of a salt of copper.

Exp. 171. — To a dilute solution of copper sulphate add a little tartaric acid, and then enough potassium hydroxide to dissolve any precipitate which forms. To half of the mixed solution add a few drops of a solution of white sugar, and warm the mixture: no change takes place. To another portion add a solution of glucose, and warm the mixture: a yellowish precipitate of a hydroxide of copper forms in the liquid, and by the boiling is converted into the red cuprous oxide. By means of this test the presence of dextrose and levulose may be shown in molasses or sirup.

385. A so-called *artificial sugar*, known as *saccharin*, and having the composition represented by the symbol $C_6H_4 \cdot CO \cdot SO_2 \cdot NH$, a derivative of benzoic acid, bearing no chemical relation to the sugars, has been prepared. It is a white, crystalline powder, which, though not readily soluble in water, has an extremely sweet taste. It has been estimated that it is 280 times sweeter than cane sugar. One part of saccharin dissolves in 200 parts of water, though it is somewhat more soluble in solutions of hydroxides and carbonates of the alkali metals.

It is somewhat used in medicine as a substitute for sugar in cases where sugar would be injurious, and it has been used also for *strengthening* glucose, and sweetening various other products. By means of one part of saccharin, one or two thousand parts of glucose could be made to taste as sweet as cane sugar.

386. There are a number of other sugars isomeric with dextrose, some of which, such as mannose, sorbose, and galactose, for example, are obtained from natural substances, while others have been prepared in the laboratory synthetically. Since there are six atoms of carbon in the molecule of each of these sugars, they are classed together as *hexaglucooses*, or as *hexoses* for short (from ξ , "six").

387. **Fermentation.** — As has already been stated in § 291, and illustrated by Exp. 138, § 292, the juice of various fruits, or aqueous solutions of dextrose or levulose, when brought into the presence of an organized substance known as *yeast*, undergo a change. The sugar is gradually converted into alcohol, while carbon dioxide escapes from the liquid. Cane sugar, as such, does not undergo this *fermentation*, but is first converted into a mixture of dextrose and levulose. Lactose, when pure, is not susceptible of fermentation, although milk can be fermented. In this case, there is formed, along with the alcohol, a quantity of an acid called *lactic acid*.

Fermented Liquors: Wines. — The various sorts of wines are produced by the spontaneous fermentation of the juice of grapes. No addition of yeast is necessary, because the ferment germs were already clinging to the grapes, or they had fallen from the air into the expressed juice (§ 291). Sweet wines are those in which there remains a portion of grape sugar which has not been converted into alcohol. Champagne is wine that has been bottled while active fermentation is going on; it contains a large amount of carbonic acid in solution.

Ale and Beer. — The seeds of many plants contain a certain proportion of a body known as starch (§ 388). By treatment with very dilute sulphuric acid, starch may be converted into grape sugar (Exp. 170, § 381). A similar change takes place in the germinating seed, under the influence of a substance called *diastase*, which is developed in the seed. Advantage is taken of this fact in the manufacture of ale and beer.

Ale and beer are generally prepared from barley. The grain is caused to germinate, by placing it under favorable conditions of moisture and temperature. When the germination has reached a certain point, it is checked, by drying the grain at a sufficiently high temperature: the product is now known as *malt*, and the process is termed

malting. The malt is crushed, and heated with water for some hours, nearly to the boiling point. It is evident that in this mashing process, when the action of the diastase occurs, additional starch obtained from other sources than barley might be thrown in, to be converted into sugar; and, in fact, rice and corn starch (perhaps corn meal) are sometimes used in this way to reinforce the barley. The infusion which results from the mashing is called *wort*; and when yeast is added to it, fermentation sets in, whereby the sugar is changed to alcohol. In order to get more alcohol and strengthen the beer, glucose is sometimes added to the wort.

The proportion of alcohol in the various beers and ales varies from 3 to 9 per cent. Beer also contains some unaltered sugar and dextrin, as well as coloring matters, and the various soluble mineral substances of the grain. The bitter taste is imparted by the addition of hops before fermentation begins, for the purpose of checking the growth of fungi other than those proper to the yeast. The foaming is caused by free carbonic acid, the peculiar consistency of the foam being apparently due to the presence of dextrin.

Other Fermented Liquors. — The juice of almost all fruits may be fermented with formation of alcoholic liquors: thus cider is the fermented juice of the apple; perry is made from pears. From the juice of the currant, gooseberry, blackberry, etc., fermented liquors are obtained, popularly called wines. The South Sea Islanders ferment the juice of the cocoanut; the Eastern nations obtain an intoxicating liquor from certain palms.

Distilled Liquors. — Absolute alcohol may be obtained by repeated distillation of any fermented liquor, and final rectification over quicklime (§ 293). When, however, the liquors are simply distilled, there is condensed with the alcohol more or less water, together with certain volatile bodies, which communicate a distinctive flavor to the product. Brandy is obtained by distilling wine, or the lees of wine; gin is spirit, flavored by distilling it with juniper berries; whisky is prepared by distilling fermented wort made from Indian corn, rye, or other grain; rum was originally made by fermenting molasses, and subjecting the product to distillation.

388. Starch ($C_6H_{10}O_5$)_n is an organized body found in wheat, maize, rice, and all other grains, in the tubers of the potato, and in the roots and stems, or in the fruits, of many other plants. Though particularly abundant in certain species and families, more or less of it is found in almost every kind of plant. The following experiment will illustrate the manner of obtaining starch from the potato, which contains, on the average, 20 per cent of it.

Exp. 173. — Reduce a clean potato to pulp by scraping or grating; mix the pulp with water, and squeeze through a linen or cotton cloth, repeating the operation several times. The woody fiber, or cellulose, of the potato, remains on the cloth, while the starch passes through the meshes and remains suspended in the *filtrate*. Allow the liquid to stand until the starch has settled; then pour off the water, and dry the residue.

389. Starch has the appearance of a white powder; but under the microscope it is seen to be made up of distinct rounded or oval grains, which vary somewhat in size and appearance, according to the particular plant from which the starch was derived. The grains of potato starch are about $\frac{1}{100}$ inch in diameter; those of wheat starch, $\frac{1}{1000}$ inch; those of rice starch are about $\frac{1}{8000}$ of an inch. Fig. 72 represents the grains of potato starch very much magnified.

390. Starch is almost entirely insoluble in water, but, when heated in water to about 70°, the granules swell and burst, and the mixture forms a jelly or paste (Exp. 59, § 112); this starch



Fig. 72.

paste is used by laundresses for stiffening linen. A characteristic property of starch is its power of forming a blue color with iodine (Exp. 59, § 112). By heating with dilute acid, starch is converted into dextrose (Exp. 170, § 381).

Inulin is a substance of the same percentage composition as starch: it occurs in the roots of the dahlia, dandelion, chicory, and other plants belonging to the family of *Compositæ*. It exists in the plant in a liquid form, it is soluble in hot water, is not colored blue by iodine, and by heating with dilute acids is converted into levulose. *Arrowroot* and *tapioca* are varieties of starch prepared from the roots of tropical plants. *Sago* is the starch obtained from the pith of the sago palm. The peculiar appearance of tapioca and sago depends on the manner in which the starch is prepared; and these varieties of starch, or, rather, successful imitations of them, are produced artificially from ordinary starch.

391. Dextrin ($C_6H_{10}O_5$)_n. — When starch is heated to about 205°, it is converted into *dextrin*, a substance of the same percentage composition as starch, but differing therefrom in many of its properties. It is soluble in water, forming a gummy solution, which is much used in the arts, particularly in calico printing, as a substitute for gum arabic and other natural gums. Large quantities of it are consumed in making beer and mucilage, and in the manufacture of adhesive stamps and envelopes. A variety of dextrin, preferred for some purposes, is prepared by dampening starch with dilute nitric or hydrochloric acid, and heating it to a temperature rather higher than 100°.

Exp. 173. — Heat carefully in a porcelain dish a teaspoonful of powdered starch, with constant stirring. It gradually turns brown. After heating for eight or ten minutes, let the dish cool; add three or four teaspoonfuls of water, and boil. A solution of dextrin will be obtained, which may be filtered from the unaltered starch. To a small portion of the solution add twice its bulk of alcohol: dextrin will be precipitated, as it is insoluble in alcohol.

392. If starch be heated for some time with water containing a small amount of sulphuric acid, the starch will be converted into dextrin; if the mixture of starch and water be heated still further, or be actually boiled, maltose will be formed, and eventually the starch, etc., will be converted into starch sugar (Exp. 170, § 381). This change of starch to dextrin and sugar takes place in nature in germinating seeds by the action of the nitrogenous substance called *diastase* (§ 387).

393. Gluten. — It has been stated that starch occurs in the different varieties of grain: its presence in wheat, as well as the presence of another body, known as *gluten*, may be shown by the following experiment: —

Exp. 174. — Wet a handful of wheat flour with enough water to make a thick dough. Wrap the dough in a linen or cotton cloth, and knead it in a slow stream of water until the water is no longer rendered turbid. The turbidity is caused by particles of starch in suspension. If a portion of the water be allowed to stand, the starch will be deposited, and may be recognized by means of the iodine test. The tough, viscous mass remaining in the cloth is gluten. In addition to these two substances, the wheat flour contains small amounts of sugars

and dextrin, which, in this experiment, are dissolved by the water, and a little oil and woody fiber which remain with the gluten.

394. **Bread.** — In the preparation of bread by means of yeast, the flour is made into a dough with water mixed with a certain amount of yeast, and the dough left in a warm place to *rise*. Fermentation sets in: the sugars and a part of the dextrin of the flour are gradually converted into alcohol and carbonic acid, and the latter being set free as a gas causes the dough to swell up and become porous. When the bread is baked, the carbonic acid expands still more, and finally escapes, together with the alcohol; but at the temperature of the oven the dough undergoes change, and the bubbles which the carbon dioxide made in it become firm and fixed, so that the bread is made light and spongy; i.e., it has acquired permanently a cellular porous structure, which permits the digestive juices of the stomach and intestines to act the more readily upon it. During the process of baking, some water is expelled from the loaf, and the starch is converted into a gelatinous condition. At the outside of the loaf further decomposition takes place, a substance like caramel being formed, which constitutes the *crust*. The crust also contains dextrin; and if the outside of the loaf be moistened, and then dried in the oven, the dextrin thus dissolved, and left again by evaporation, produces a smooth, shining surface.

Leaven, or dough left over from a previous baking, is sometimes used for raising bread, instead of yeast. It is objectionable, in that it is apt to contain, beside the yeast plant, other kinds of ferments; such, for example, as those which produce lactic acid. To neutralize the acidity, saleratus is commonly added to leavened dough, an incidental advantage being gained by so doing, in that the carbon dioxide, liberated from the saleratus by the lactic acid, helps to puff up the dough. There is always a risk however, that there may be added more than enough saleratus to neutralize the acidity; and in this event the bread takes on a yellow color, and has an alkaline taste.

395. **Cellulose** ($C_6H_{10}O_5$)_n occurs in all plants and in all the various parts of the plant. It is one of the chief constituents of the walls or outside coating of the cells of which every vegetable organism is made up, and occurs in a great variety of forms. It would be more accurate, indeed, to speak of *the celluloses* rather than of *cellulose*. The groundwork of succulent fruits (like the apple and pear), of roots (like the turnip and beet), as well as of all varieties of trees, even the box and the *lignum-vitæ*, is cellulose. Linen and cotton are nearly pure cellulose, the fibers being made up of long cells; but in almost

all cases the cellulose is accompanied by another substance, *lignin* or *lignic acid*, which incrusts the interior of the cells, and predominates in the case of the harder woods and in the shells of the different sorts of nuts. This incrusting substance is of uncertain composition, as it never has been obtained sufficiently pure for analysis; but it is known to contain a larger percentage of carbon than cellulose does. The finest kinds of filtering (unglazed) paper are nearly pure cellulose. In Exp. 172, § 388, the substance remaining in the cloth was mainly cellulose.

Wood Paper. — The manufacture of paper from wood pulp has of late years become an important branch of chemical industry. An inferior kind of coarse paper might be prepared from the pulp obtained by simply shredding mechanically the wood of various kinds of trees, such as that of the conifers, poplars, tulip tree, etc.; but, in order to prepare a really useful pulp, chemical agents must be resorted to for the purpose of freeing the cellulose of the wood from various substances which encumber it. The processes now in use for preparing wood pulp are the *caustic-soda process* and the *bisulphite process*. In the caustic-soda process, the wood is chopped up, crushed, and heated under pressure with caustic soda; the hot, strong alkali dissolves resins, coloring matters, albuminoids, and gum, together with a part of the lignin or incrusting matter; and there is left a nearly pure fiber, though the strength of this fiber is apt to be somewhat weakened by the action of the soda. In the bisulphite process, the crushed wood is extracted with hot water, and heated for a number of hours to 118° under pressure, either with calcium acid sulphite or with magnesium acid sulphite, which act on the lignin to form sulpholignic salts, which dissolve, while there is left a pure white fiber in larger amount, and of superior strength to that obtainable by the soda method.

The percentage composition of cellulose is the same as that of starch, dextrin, and inulin, and would be most simply expressed by the formula $C_6H_{10}O_5$. It is probable, however, that the true formula of cellulose is some higher multiple of these numbers, not less than $C_{18}H_{30}O_{15}$, possibly $C_{180}H_{300}O_{150}$.

396. Pure cellulose is a white substance, insoluble in water, alcohol, or dilute mineral acids. Some varieties dissolve at once, with but little change, in strong hydrochloric acid in which one half its weight of zinc chloride has been dissolved. Strong alkalies decompose cellulose, and finally form oxalic acid (§ 410). Strong sulphuric acid dissolves it; and, on diluting the solution and boiling, the cellulose is changed to dextrose,

and in some instances to other kinds of sugars. By short contact with sulphuric acid of a particular strength, cellulose is converted into a semitransparent, tough substance resembling animal membrane. Paper thus treated is changed into a substance known as *vegetable* or *artificial parchment*.

Exp. 175.— To 10 cc. of water in a porcelain dish add slowly, with constant stirring, 25 cc. of strong sulphuric acid. When the mixture has become perfectly cold, immerse in it a piece of filtering paper. Allow the paper to remain in the liquid for 15 or 20 seconds; then remove, and rinse thoroughly, to remove the acid, first with pure water, then with water containing a little ammonia, and finally with pure water again. The paper is converted into vegetable parchment. If the first experiment be not successful, repeat with fresh pieces of paper, varying the time of immersion until a good result is obtained.

397. By treatment with a mixture of nitric and sulphuric acids, cellulose is converted, without change of form, into compounds known as *cellulose nitrates*, *nitrocellulose*, *pyroxylin* or *guncotton*. Most of these compounds are very explosive, although not nearly as much so as nitroglycerin, which is prepared from glycerin in a similar manner. In the air, guncotton burns with a sudden flash, without smoke. If burned in a confined space, it produces explosive effects similar to those produced by gunpowder.

Guncotton is, chemically speaking, cellulose in which a certain number of atoms of hydrogen have been replaced by the radical NO_2 ; but the composition and properties of the product differ, according to the strength and proportions of the acids used in its formation. Several distinct varieties of nitrocellulose are made use of in the arts.

Collodion is the name given to the solution, in a mixture of alcohol and ether, of those varieties of cellulose nitrate which contain no more than two, three, or four of the NO_2 groups. When this solution is exposed to the air in a thin layer, the solvent rapidly evaporates, and leaves a transparent, tenacious film, which has been made use of both in surgery and in photography. When collodion is brushed over a small wound or scratch, it disinfects the wound, and shields it from contact with the air; i.e., this solution destroys any microorganisms which may be present, and the film prevents others from coming in from the air, so that the wound, if it be small, will quickly heal. Collodion is used also in admixture with various solvents for making delicate varnishes, or lacquers, to be put upon fine metal work.

Celluloid.—By incorporating with guncotton a certain proportion of camphor, either by means of solvents or by heating a mixture of the materials, there is obtained a substance called *celluloid*, which is plastic when soft, but solidifies to a hard, elastic, ivorylike material. It can be colored in many ways, and is largely used as a substitute for ivory or tortoise shell. It burns freely when touched with a lighted match.

398. Gums.—*Gum arabic* is a familiar example of a class of bodies which occur in the juice of almost all plants. It exudes freely from several species of acacia, and is valuable chiefly because it forms with water an adhesive paste. It finds many applications in medicine and in the arts, in making confectionery and inks, and in calico printing.

The gums are soluble in water, but insoluble in alcohol, as may be illustrated in the case of gum arabic by the following experiment:—

Exp. 176.—Dissolve 10 g. of gum arabic in 75 cc. of water. The solution is facilitated by powdering the gum arabic, mixing it with clean, dry sand, and stirring the mixture from time to time. When solution has been effected, allow the sand to settle, and pour off the liquid.

To a portion of the solution thus prepared, add half its bulk of alcohol: the gum is reprecipitated.

399. Gum arabic is a mixture of the calcium and potassium salts of arabic acid. Calcium and potassium arabates are soluble in water: many other arabates are insoluble in water.

Exp. 177.—To a portion of the solution of gum arabic of Exp. 176, add an ammoniacal solution of lead acetate (prepared by adding to an aqueous solution of lead acetate ammonia water in quantity insufficient to produce a precipitate): a white precipitate of an arabate of lead is formed.

By the action of hot dilute acids, arabic acid, or *arabin*, as it is often called, changes to a kind of sugar called *arabinose* ($C_5H_{10}O_5$), much in the same way that starch changes to dextrose under similar conditions.

To the class of gums belong the exudations from trees like the cherry, peach, and plum. *Gum tragacanth* is a familiar example of these bodies. The substances which exude from pines and similar trees, often called gum, as *spruce gum*, for example, belong to a different class of bodies,—that of the resins (§ 403).

Gum tragacanth is a modification of ordinary gum. When treated with water, it swells up, but does not dissolve: 4 or 5 g. of this gum are sufficient to convert a liter of water into a pasty mass.

400. Hemicelluloses.—Those portions of the cellular tissue which, although insoluble in water, dissolve on being boiled in dilute acids, may conveniently be classed as *hemicelluloses*, to distinguish them from cellulose proper, which is not soluble to any extent in dilute acids. Among hemicelluloses may be placed various substances, which were formerly regarded either as tender cellulose, or as *pectose*, or *pectin substances*. Even the gums will naturally fall into this category: the class will include, also, a substance, closely related to the gums, that has been called *wood gum*, *metapectic acid*, *xylin*, *xylan*, etc., which is found in very considerable quantity in wood and straw, and which occurs in the tissues of most plants. On boiling this wood gum, or *xylan*, with dilute sulphuric acid, a sugar, called *xylose*, is obtained, which is isomeric with the sugar (arabinose, § 399) obtained from gum arabic by similar treatment. These two sugars, xylose and arabinose, have the formula $C_5H_{10}O_5$, and are classed together as *pentaglucooses*, or *pentoses* (from *πέντε*, “five”).

The flesh of many edible roots, such as beets and turnips, and that of squashes, pumpkins, cabbages, and berries, as well as of unripe apples and other fruits, contains, along with some cellulose proper, *hemicelluloses* insoluble in water, but which become soluble in some part as the fruit ripens. They are made soluble also by the action of weak acids or other chemical agents, with formation of gums and jellies, to which have been given the names *pectin*, *pectic acid*, etc. By boiling with dilute acids, all these pectin substances may be converted into sugars. The name *pectose* was formerly applied to the insoluble hemicelluloses in roots and fruits.

Exp. 178.—To prepare the substance known as *pectin*, reduce several white turnips or beets to pulp by grating. Inclose the pulp in a piece of cotton cloth, and wash by squeezing in water, until all the soluble matters have been removed, or until the water comes off nearly tasteless. To the washed pulp add enough dilute hydrochloric acid (1 part, by measure, of the strong acid to 15 parts of water) to saturate the mass, and allow it to stand for 48 hours. At the end of that time, squeeze out the acid liquid, filter it, and add an equal bulk of alcohol. Pectin will separate as a gelatinous, stringy mass.

401. The viscid, gummy juice which oozes from baked apples is a strong solution of pectin. The various sorts of fruit jellies are composed of other products of the transformation of the hemicelluloses in the fruit.

402. The Carbohydrate Group.—It will be noticed that the foregoing substances, or groups of substances, — viz., the sugars,

starch, dextrin, gum, etc., — all contain hydrogen and oxygen in the same proportions that these elements are combined in water. The formula of starch, for example, might be written empirically ($6C + 5H_2O$)_x; that of cane sugar, $12C + 11H_2O$; and so on. On this account, the term *carbohydrates* is often applied to the whole class of vegetable substances comprised in the above-mentioned groups.

Several chemists have suggested (§ 374) that the formation of the carbohydrates in plants may depend on the polymerization of formic aldehyde. Thus $6(CH_2O)$ is equal to $C_6H_{12}O_6$, which is the formula of dextrose and its isomers; and it may be said, in general, that xCH_2O can be condensed to $(CH_2O)_x$, and that the various carbohydrates may be built up, step by step, by the condensation of simpler molecules. There are sugars, now actually known, which might be referred to seven different degrees of condensation of formic aldehyde: viz., to $3(CH_2O)$, $4(CH_2O)$, $5(CH_2O)$, $6(CH_2O)$, $7(CH_2O)$, $8(CH_2O)$, and $9(CH_2O)$; and these groups have been named respectively the *triose*, *tetrose*, *pentose*, *hexose*, etc., groups, in accordance with the number of atoms of carbon which they contain. A sugar called *glycerose* (glycerin aldehyde, $C_3H_6O_3$), obtained from glycerin, belongs to the first of these groups; and one called *erythrose* ($C_4H_8O_4$), obtained from the tetra-acid alcohol erythrit, belongs to the second or tetrose group. Members of the third and fourth groups (i.e., pentoses and hexoses) have just now been described; and a number of sugars of the fifth, sixth, and seventh groups have been prepared artificially.

Starch, dextrin, and cellulose, as well as sucrose ($C_{12}H_{22}O_{11}$) and its isomers, may be regarded as polyglucoses which have been formed by way of condensation. In this point of view, the sucroses have been called *disaccharids*; while *raffinose* ($C_{18}H_{32}O_{16}$), a sugar formed at beet-sugar works, has been classed as a *trisaccharid*. Those polyglucoses which, on being heated with acids, yield hexoses, are often spoken of as *hexosans*; while the hemicelluloses, such as the gums and wood gum (xylan), that yield pentoses when heated with acids, are called *pentosans*.

403. Resins. — Most resins exude, together with essential oils, either spontaneously from trees or shrubs, or from incisions made in the stems or branches. Common rosin is the resin of turpentine (Exp. 154, § 325). It burns with a smoky flame, and is used in the preparation of lampblack (§ 237) and cheap varnish. When rosin is subjected to dry distillation, it yields a distillate, rosin oil, the more volatile part of

which is used as a solvent by varnish makers. The heavier rosin oil is used instead of linseed oil in the manufacture of printer's ink, and for mixing with animal and vegetable oils. By stirring the heavier oil up with milk of lime, rosin grease is obtained, a mixture sometimes used for lubricating wagon wheels and the bearings of heavy machinery. Gum copal, mastic, sandarach, and shellac are resins. The resins are insoluble in water, but dissolve in alcohol, wood naphtha (§ 303), naphtha, and oil of turpentine. The solutions thus obtained are called *varnishes*. When exposed in a thin layer to the air, the solvent evaporates, leaving a transparent coating of the resin, which protects the varnished surface from air and moisture.

Exp. 179. — Powder 3 g. of shellac, mix it with a quantity of clean sand, and pour upon it 30 cc. of alcohol. Allow the mixture to stand until the shellac has dissolved. Pour a portion of the solution into water: the shellac is precipitated, as it is insoluble in water.

404. The resins seem, in many cases, to be formed by the oxidation of the essential oil of the plant by which they are produced; and it is a familiar fact, that, when oil of turpentine is exposed to the air, it absorbs oxygen, and is converted into a sticky, resinous substance. During the oxidation, ozone is produced, and its effects are manifested by its bleaching action on the corks of the bottles in which oil of turpentine is kept.

The resins are made up in the main of several acid bodies, of which resinic acid is the principal. By the action of bases on resin, bodies called *resinates* are formed. Thus sodium resinate, formed by the action of caustic soda on common rosin, is used in the manufacture of some kinds of soap: it is soluble in water, and valuable on account of its detergent properties. Lead resinate is insoluble in water and alcohol.

Exp. 180. — Dissolve a small amount of powdered rosin in alcohol; dissolve also a portion of crystallized lead acetate in 10 times its bulk of alcohol. Mix the two solutions, and observe the formation of a bulky, white precipitate of lead resinate.

405. **Caoutchouc**, or **India rubber**, the solidified juice of certain tropical plants, is a mixture of several hydrocarbons of the formula $(C_{10}H_{16})_n$. It is insoluble in water, but when treated with ether, chloroform, carbon disulphide, oil of turpentine, or benzol, it swells up in a very remarkable manner, and finally forms a sort of solution.

Exp. 181.—Into a small bottle put several teaspoonfuls of oil of turpentine, and add a few clippings of sheet caoutchouc. Cork the bottle, and allow it to stand for some time. The caoutchouc swells up to many times its original bulk, and eventually dissolves.

406. Caoutchouc, at ordinary temperatures, is elastic, and freshly cut edges unite permanently when strongly pressed together. At higher temperatures, it is so soft that it can be kneaded; and at lower temperatures, it is hard, stiff, non-adhesive, and nonelastic. By mixing it with some 10 per cent of sulphur, and heating the mixture to about 125° , caoutchouc may be made to take up and combine with a certain proportion of the sulphur, forming what is called *vulcanized India rubber*. This substance preserves its consistency and its elasticity through all ordinary changes of temperature. By mixing the caoutchouc with a larger proportion of sulphur (30 or 35 per cent), and heating to a higher temperature, there is obtained a product which resembles horn, called *hard rubber*, *vulcanite*, or *ebonite*. India rubber is largely used in the manufacture of waterproof clothing, tubing for conveying liquids and gases, combs, buttons, picture frames, and a great variety of other articles. Instead of sulphur, metallic sulphides are sometimes used for vulcanizing caoutchouc.

407. **Gutta-percha** is a substance analogous to India rubber, and, like it, seems to consist in good part of hydrocarbons of the formula $(C_{10}H_{16})_n$. It is tough and hard at ordinary temperatures, but becomes soft even when moderately heated, and at 50° it can be kneaded and molded. Gutta-percha has important uses as a material for making molds, and large quantities of it are employed for insulating submarine telegraph cables.

408. **Amber** is one of a number of fossil substances resembling the resins. Amber is found principally along the shores of the Baltic, but also occurs in beds of lignite in other localities. It becomes highly electric on friction. Chemically, it is a mixture of several resinous bodies; it also contains a peculiar acid called *succinic acid*. Only about an eighth part is, in its natural state, soluble in alcohol; but, after fusion, it dissolves quite readily, and is used in the preparation of varnish.

409. Vegetable Acids.—Among the important products of the vegetable kingdom are the *organic acids*, which occur ready formed in plants, either in the free state or in combination, as salts of certain metallic elements or radicals. The occurrence of the salts of several of the fatty acids in the oils of plants has already been noticed. The salts of oleic acid (§ 314), and other acids classed with it, also exist in vegetable fats and oils. The acids which are to be considered in this place generally occur as salts of calcium or potassium.

410. Oxalic acid ($C_2H_2O_4$) occurs as potassium oxalate and calcium oxalate in the juice of the sorrel, rhubarb, and many other plants. Calcium oxalate, though insoluble in water, appears occasionally to be somewhat soluble in the juices of the plant; though more commonly it is found in the cells of plants as microscopic crystals. Since it possesses well-marked acidity, oxalic acid acts as a corrosive poison when taken internally in any considerable quantity, though it is apparently harmless in small amounts or when largely diluted. The best antidote is chalk (calcium carbonate) or magnesia, as the oxalates of calcium and magnesium are insoluble compounds.

411. On the large scale, oxalic acid is prepared by making a thick paste of sawdust with a strong solution of caustic potash and caustic soda, and heating the mixture on iron plates. The woody fiber is converted into oxalic acid, and sodium and potassium oxalates are formed, from which the acid is extracted. On a small scale, oxalic acid is best prepared by the action of nitric acid on starch or sugar.

Exp. 182.—In a flask of 500 cc. capacity heat gently 100 cc. of nitric acid of 1.38 specific gravity, and 10 g. of starch. The experiment should be performed where there is a good draught of air, as nitrous fumes are copiously evolved. When the evolution of the fumes has nearly ceased, the solution is transferred to an evaporating dish, and slowly evaporated to about one sixth its bulk. On cooling the solution, oxalic acid will be obtained in transparent crystals.

412. Oxalic acid occurs in crystals having the formula $C_2H_2O_4 + 2 H_2O$. The crystals lose the water of crystallization when dried at 100° , and at the ordinary temperature of the air they effloresce somewhat. The crystals are much more

soluble in hot than in cold water. Oxalic acid dissolves the metallic oxides with facility, forming oxalates. On this fact depends its use in cleaning articles of brass and copper, and in removing spots of iron rust and ink.

Exp. 183. — Dip a piece of white cloth in common writing ink, and when dry, immerse it in a solution of oxalic acid, made by dissolving 2.5 g. of oxalic acid in 50 cc. of water. Then rinse the cloth in water: the color will be discharged.

Many kinds of writing ink owe their color to a tannate of iron (§ 420), which, on exposure to the air, becomes nearly insoluble in water. The oxalic acid destroys this compound, and forms, with the iron, a soluble combination.

413. If the formula of oxalic acid ($C_2H_2O_4$) be written $H_2O.C_2O_3$, the existence of an anhydride (C_2O_3) might be inferred, an oxide of carbon intermediate between CO and CO_2 . Such anhydride has, however, never been obtained. When oxalic acid is treated with strong sulphuric acid, it is broken up, the sulphuric acid retaining the H_2O , while the C_2O_3 divides into CO and CO_2 . In fact, this is a common way of making carbon monoxide. By distilling alcohol with oxalic acid, "oxalic ether," or ethyl oxalate, is obtained $(C_2H_5)_2C_2O_4$.

414. **Malic acid** ($C_4H_6O_5$) occurs abundantly in unripe apples, and in most acid fruits, such as the gooseberry and currant. As potassium malate, it occurs in the rhubarb; and crystals of this salt may be obtained by evaporating the juice of the leaf stalks. Calcium malate occurs in sumach berries and in the sap of the maple. In boiling down the maple sap to obtain the sugar, fine, hard crystals of calcium malate often separate, as a kind of sand. Malic acid may be obtained in crystals, extremely soluble in water, which deliquesce in moist air.

415. **Lactic acid** ($C_3H_6O_3$) is found in sour milk, having been formed there by the fermentation of the milk sugar (§ 379). It is prepared as a commercial product in this country by causing a microscopic organism, known as the *lactic ferment*, to act upon glucose. Large quantities of preparations of it are used as substitutes for lemon juice and extract of lemon, and much of it is used also in several processes of dyeing.

416. **Tartaric acid** ($C_4H_6O_6$). — Tartaric acid occurs in a great variety of plants. The commercial supply is obtained from the grape. All varieties of wine, during fermentation, deposit, on the insides of the casks, a crust called *argol*. This argol, or

crude tartar, is a potassium acid tartrate, commonly called *bitartrate of potash*; when purified, it is called *cream of tartar*. From argol, or cream of tartar, tartaric acid itself may be obtained in transparent crystals, which are permanent in the air.

Exp. 184. — Dissolve 20 g. of cream of tartar in 150 cc. of hot water, to which 10 cc. of strong hydrochloric acid have been added. To the solution add milk of lime (made by stirring 20 g. of slaked lime, calcium hydroxide, into 100 cc. of water) until the solution shows a distinctly alkaline reaction. Insoluble calcium tartrate settles to the bottom of the liquid, and should be collected on a filter and washed. Transfer this calcium tartrate to a flask, add 100 cc. dilute sulphuric acid (made by adding 10 g. oil of vitriol to 100 cc. water), and boil for some minutes. The sulphuric acid causes the formation of calcium sulphate, and free tartaric acid is left in the liquid. The insoluble calcium sulphate is removed by filtration. The filtrate is concentrated, by evaporation over the lamp, to the bulk of 20 cc., and allowed to cool. Crystals of tartaric acid separate from the liquid. These crystals are drained from the mother liquor, and pressed between pieces of filter paper. They may be purified by dissolving them in half their weight of boiling water, and allowing the solution to cool, when a considerable part of the acid crystallizes out again.

417. Tartaric acid finds important applications in the art of dyeing, and many of the *tartrates* are important compounds. Rochelle salt is a sodium potassium tartrate; tartar emetic is an antimony potassium tartrate: both these salts are used in medicine. The so-called *Sedlitz* or *Rochelle powders* contain a mixture of Rochelle salt and sodium acid carbonate in one paper, and tartaric acid in the other. When the contents of the two papers are mixed in water, carbon dioxide is set free, and Rochelle salt remains in solution. *Soda powders* contain sodium acid carbonate in one paper, and tartaric acid in another.

Exp. 185. — Dissolve 10 g. cream of tartar in 175 cc. of hot water, and to the solution add a strong solution of sodium carbonate as long as the addition produces effervescence. Evaporate the solution over the lamp to the bulk of 20 cc., and then allow it to cool. Crystals of Rochelle salt will be obtained.

418. Citric acid ($C_6H_8O_7$) occurs very abundantly in the juice of the lime and the lemon, and has been found in the tomato and in most acid fruits. It may be obtained crystallized, with

one molecule of water, in large transparent crystals. It has a sour but rather agreeable taste. It is used by calico printers, and to some extent in medicine, especially as magnesium citrate.

419. Tannic Acid. — *Tannin* is the general name applied to an astringent principle contained in the leaves and bark of many forest trees, such as the oak, hemlock, and pine. Similar substances occur in the leaves and bark of many fruit trees, in the roots of certain plants, as well as in coffee and tea. These substances possess an acid reaction, and several distinct acids have been identified in them. The tannin derived from gallnut is called *gallotannic acid*; that from oak bark is called *quercitannic acid*; that from coffee, *caffetannic acid*.

420. The principal applications of tannic acid in the arts are for dyeing and mordanting cloths, for making writing ink, and for tanning leather.

Exp. 186. — Boil 10 g. of powdered nutgalls in about 60 cc. of water for several hours, replacing from time to time the water lost by evaporation: a solution of tannic acid is thus obtained. Allow the mixture to settle, and decant the clear liquid into a clean bottle. To a portion of this solution add a few drops of a solution of copperas (ferrous sulphate). A violet-colored precipitate is formed, which gradually changes to black: it is an iron tannate. If the solution of tannic acid were made viscous by the addition of a little gum, the precipitate would remain suspended in the liquid. Common ink is made from these materials.

Exp. 187. — To another portion of the tannic acid solution add a few drops of a solution of gelatin or isinglass. A copious white gelatinous precipitate falls.

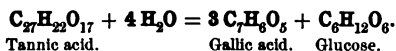
On the property just illustrated, of uniting with gelatinous matters to form insoluble compounds, depends the use of tannic acid in tanning. If a piece of rawhide from which the hair has been removed be immersed in an infusion of oak bark, the gelatinous matters of the hide gradually remove the tannic acid from the solution, and combine with it to form an insoluble compound, which remains in the structure of the hide. The skin thus altered is leather.

421. In Exp. 186, § 420, it was seen that a solution of a salt of iron was blackened by the addition of a solution of

tannic acid derived from gallnuts. This reaction may be made use of as a test to demonstrate the presence of tannic acid.

Exp. 188. — Boil a few tea leaves in a small amount of water, and to the liquid add a drop or two of a solution of copperas. The liquid is blackened, and after a time a black precipitate of iron tannate subsides. The presence of tannic acid may be shown similarly in coffee, in hemlock bark, in horse-chestnut husks, etc.

422. Gallic Acid. — The gallnuts used in Exp. 186, § 420, are excrescences produced on a species of oak by the punctures of a certain insect. Beside tannic acid, the nutgalls contain a small percentage of another acid, *gallic acid*. Gallic acid may also be produced by boiling a solution of tannic acid (from nutgalls) with dilute sulphuric acid. The composition of tannic acid is $C_{27}H_{22}O_{17}$. When boiled with dilute sulphuric acid, it unites with the elements of water, and forms gallic acid and glucose (§ 381), —



Tannic acid is the representative of a class of bodies which, by a reaction analogous to that represented above, yield glucose: they are hence called *glucosides*.

423. The vegetable alkaloids, or organic bases, occur in small quantities in various plants, of which they constitute the medicinal or poisonous principles. They occur in combination with some acid which is generally peculiar to the particular plant in which they are found. They are only slightly soluble in water, but are readily dissolved by alcohol. They resemble ammonia in containing nitrogen, in having an alkaline reaction, and in uniting directly with acids to form salts, which, as a rule, crystallize readily.

424. Theine, or **caffeine** ($C_8H_{10}N_4O_2 \cdot H_2O$), is a crystalline, slightly poisonous substance, which may be obtained from tea and coffee. When taken internally, it acts to produce nervous instability and sleeplessness, and to excite increased action of the heart. A closely related substance, theobromine, occurs in the cacao bean.

425. Morphine, or **morphia** ($C_{17}H_{19}NO_3 \cdot H_2O$), is an invaluable medicament obtained from opium, which is the dried juice of unripe poppy heads. When given in small doses, morphine

has a sedative effect, but in large doses it acts as a narcotic poison.

Nicotine ($C_{10}H_{14}N_2$) is the chief alkaloid in tobacco, and is a very violent poison.

Strychnine, or strychnia ($C_{21}H_{22}N_2O_2$), is a highly poisonous alkaloid which occurs in the St. Ignatius bean and in the nux vomica, associated with brucine ($C_{28}H_{26}N_2O_4 \cdot 4H_2O$). Of the two, strychnine is the more violent poison, although both are very powerful in their effects on the living organism.

The bark of the cinchona, a tree found native in Peru, contains several bases, of which the most important are *quinine* ($C_{20}H_{24}N_2O_2 \cdot 3H_2O$) and *cinchonine* ($C_{19}H_{22}N_2O$). Quinine possesses valuable medicinal properties, and is used as a febrifuge; cinchonine is also employed as a medicine, but is of less value than quinine.

Cocaine ($C_{17}H_{21}NO_4$), an alkaloid extracted from the leaves of the coca, a South American plant, has very remarkable anæsthetic properties, and is much used by surgeons, in the form of *hydrochlorate of cocaine*.

426. Toxines, also called **ptomaines**, are alkaloidlike bodies, several of which are highly poisonous, that are found either in decaying animal matter, or within the tissues of living animals that are suffering from some forms of disease.

Toxines are produced by the action of various microorganisms, such as those that cause diseases, and those concerned in processes of putrefaction. It often happens that men are poisoned by a trifling cut received while skinning a dead animal, or by drinking milk which has slightly "turned;" for in this case the warmth of the body may promote a very rapid development of the microorganisms, by means of which the toxines are produced. Occasionally whole families are made ill by eating sausages, corned beef, lobster salad, ice cream, or the like, because the animal matter had begun to suffer decomposition, and had become charged with a toxine. So, too, in many kinds of diseases, such as diphtheria and typhoid fever, the patient, while resisting the palpable local inflammation, may succumb to the poisonous action of a toxine, which is one result of the disease. The toxines which may occur in foods are all the more dangerous, because many of them, unlike the microorganisms by which they are produced, are not destroyed by processes of salting, cooking, smoking, or freezing. Once formed, they are highly refractory. It is an error to suppose

that meat which has been kept too long can be made fit for food by corning it.

It has long been known that many kinds of mushrooms are poisonous, and that other kinds are sometimes poisonous when over-ripe or partially decayed; and it has been discovered that poisonous mushrooms contain toxins analogous to those in spoiled meat, some of which are extremely dangerous. It would appear that toxins are habitually formed as an incident to the life of fungi of many kinds, both large and small (microscopic).

427. Coloring Matters of Vegetable and Animal Origin. — Almost every plant contains coloring matter of some sort, and many of the materials used in dyeing are of vegetable origin. It is noticeable, that, while most coloring matters occur ready formed in the plant, there are some which result from the action of air, or some other chemical agent, upon natural products. Only a few of the known vegetable coloring matters can be here mentioned.

428. Indigo. — Of the vegetable dyes, one of the most important, and one which possesses considerable chemical interest, is *indigo*, which is used, as is well known, in producing a very permanent blue color. As it occurs in commerce, indigo contains a blue coloring matter, which, when purified, is known as *indigotin*, or *indigo blue* ($C_{16}H_{10}N_2O_2$). This blue coloring matter does not occur ready formed in the plant, but is produced by a sort of fermentation. Indigo blue is insoluble in water or in alkaline liquids, but dissolves in fuming sulphuric acid (§ 161), forming a deep blue solution.

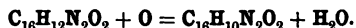
Exp. 189. — Upon 1 g. of finely powdered indigo pour 6 g. of fuming sulphuric acid, and let the mixture stand for some hours in a warm place. On the addition of water, a deep blue solution is obtained. Ordinary strong sulphuric acid will dissolve indigo; but it is necessary to take a much larger quantity (in this case, about 12 or 14 g.), and to heat the mixture to about 60°. Moreover, when thus heated, a portion of the blue coloring matter is destroyed.

429. The deep blue liquid formed by the action of sulphuric acid on indigo contains at least two acid compounds. The solution is, however, commonly spoken of as *sulphindigotic acid*, and is used just as made, or partially neutralized with sodium or potassium carbonate, in dyeing the color known as Saxon blue, and in the preparation of various sorts of bluing.

430. When blue indigo is treated with reducing agents, it is converted into a colorless compound, soluble in alkaline liquids, and known as *white indigo*. On exposure to the air, the white indigo is reconverted into insoluble indigo blue.

Exp. 190. — Into a test tube put as much finely powdered indigo as can be taken on the point of a small penknife, and half a teaspoonful of fine zinc filings (*zinc dust* is best, if it can be obtained). Pour into the test tube two teaspoonfuls of a moderately strong solution of caustic soda, and heat the mixture: the caustic soda acts upon the zinc, and hydrogen is set free; by the action of the nascent hydrogen, the indigo blue is converted into white indigo, and the white indigo dissolves in the alkaline liquid, forming a yellowish solution.

The formula of white indigo is $C_{16}H_{12}N_2O_2$. When an alkaline solution of white indigo is exposed to the air, it is converted into indigo blue, —



Exp. 191. — Pour out a portion of the solution of the preceding experiment into a shallow dish, and observe, that, in contact with the oxygen of the air, insoluble indigo blue is formed.

Exp. 192. — Dip a piece of white cloth or filter paper into the liquid remaining in the test tube. As soon as the moistened cloth or paper comes out into the air, it will turn blue.

The experiment illustrates the method actually employed, to some extent, in dyeing with indigo. Other reducing agents are also used (very commonly, a mixture of slaked lime and copperas), the action of which will be better understood hereafter. The cloth dipped into the solution of white indigo becomes thoroughly impregnated with this solution; and when the indigo blue is formed, it is formed within and among the fibers of the cloth, so that the color is *fast*.

431. The synthesis of indigotin has been effected as a result of investigations as to its chemical conduct and relations, and it is now manufactured on a large scale.

432. *Cochineal* is an insect which lives in hot countries, on a species of cactus. This insect contains a coloring matter, *carminic acid* ($C_{17}H_{18}O_{10}$), which is soluble in water and in alcohol, and dissolves in caustic alkalies, also, to a fine red color. It is a glucoside (§ 422), and can be decomposed into “*carmine red*” ($C_{11}H_{12}O_7$) and a sugar ($C_6H_{10}O_5$).

Exp. 193. — Boil 2 g. of crushed granules of cochineal in 75 cc. of water for some minutes. Filter the colored solution, and preserve it for use in subsequent experiments.

Among other organic coloring matters used in dyeing are the various red dyestuffs, *Brazil wood*, *logwood*, and *safflower*.

433. Madder. — At one time the root of a plant called *madder* was a very important dyeing material. It owed its value chiefly to a constituent called *alizarin* ($C_{14}H_8O_4$); but it was observed, some years since, that reducing agents convert alizarin into anthracene (§ 367), and methods were soon devised for making alizarin and the other madder colors from anthracene. The introduction of these artificial dyestuffs has well-nigh destroyed the old significance of the madder root.

434. Yellow dyestuffs are *quercitron*, obtained from the bark of a variety of oak; *fustic*, from the wood of a West-Indian tree; *turmeric*, from the root of an East-Indian plant; and a coloring matter obtained from "Persian berries." *Annato* is obtained from the fleshy pulp which surrounds the seeds of a certain South-American tree. It is used to a small extent for dyeing silk, and to a large extent for coloring butter and cheese, as well as oleomargarine. Certain species of lichens also yield coloring matters: the dyestuffs known as *archil*, *cudbear*, and *litmus* are derived from such sources.

435. Dyeing. — One method of dyeing fibers or fabrics of animal and vegetable origin has been illustrated by Exp. 166, § 363, in which simple immersion of the wool in the solution of picric acid sufficed to give it a yellow color.

Exp. 194. — Into a warm solution of picric acid, prepared as directed in Exp. 166, § 363, put a piece of cotton cloth or a skein of cotton yarn. After the cotton has been immersed in the solution for some time, take it out, and rinse it with water. It will be found that the cotton is not colored.

This experiment illustrates a very important difference between the fibers of vegetable and those of animal origin. Of almost all the vegetable coloring matters, it is true that they do not directly produce fast colors on cotton or linen, while they readily color articles of silk or wool.

Exp. 195. — Prepare a solution of the coloring matter of logwood by dissolving 1 g. of extract of logwood in 75 cc. water. Allow the liquid to stand for a short time, until it becomes nearly clear, and

then decant it from any insoluble matter which may subside. Place a quantity of the nearly clear solution in a porcelain evaporating dish, put into it a piece of cotton cloth 5 or 6 cm. square, and boil for some 10 minutes. On removing the cloth, it will be found possible to wash out most of the dye, leaving the cloth only slightly colored.

Exp. 196. — Into a quantity of logwood solution, equal to that employed in the last experiment, put a piece of cotton cloth, 5 or 6 cm. square, which has previously been soaked, first in a solution of common alum, and then in ammonia water. Boil the solution as in the previous experiment. When the cloth is removed, it will be found to be quite strongly colored.

This experiment illustrates the fact that it is possible to impregnate the cloth with certain substances which have the power of dragging in the coloring matter and holding it firmly. Such substances are called *mordants*, and, as they are generally compounds of some of the metals, their action will be better studied hereafter (§ 574).

436. Physiological Chemistry. — The study of the various fluids and solids occurring in the living animal, and concerned in the processes of circulation, respiration, and digestion, belongs more particularly to that branch of the science designated as *physiological chemistry*, which is properly treated of in special text-books.

The chemical relations of the substances concerned in the vital functions are, generally speaking, somewhat intricate and obscure, and many of the substances themselves are extremely complex: thus to *albumin* has been assigned the formula $\text{C}_{72}\text{H}_{112}\text{N}_{18}\text{SO}_{22}$, though a formula such as this can be regarded only as a rough approximation to the truth. Bodies of like complexity occur also in vegetables, although the mass of the plant is made up, as we have seen, of substances comparatively simple in composition. The more particular study of the chemical phenomena involved in the growth, nutrition, and decay of plants, belongs to *agricultural chemistry* and to *vegetable physiology*.

In this place, brief mention will be made of a few of the more important compounds, occurring in animals and plants, which have not already been considered.

437. Albumin, or albumen, occurs abundantly in many of the fluids and soft solids of the animal body. It is most familiar as the *white* of the eggs of birds; it is found also in consider-

able proportion in the blood, although blood albumin differs in some of its characters from egg albumin. The most striking properties of albumin are its solubility in water and its coagulation by heat and other agents: these properties may be exhibited with fresh white of egg.

Exp. 197. — Beat or whip the white of an egg, to destroy the transparent membrane of the cells in which the albumin is held, and agitate a portion of it with water: it dissolves readily.

Exp. 198. — Add strong alcohol to a portion of the solution obtained in Exp. 197: the albumin is coagulated.

Exp. 199. — Place a little of the albumin in a test tube, put the tube into water contained in a beaker or evaporating dish, and heat the dish. Observe that the albumin coagulates some time before the water is hot enough to boil; namely, at about 60° .

Albumin is a very complex compound of carbon, hydrogen, and oxygen, and contains also a certain proportion of nitrogen and sulphur. A body of similar composition occurs in vegetables, and is called *vegetable albumin*. To the presence of sulphur in albumin, and in a somewhat similar body which occurs in the yolk of eggs, is due the peculiar odor of rotten eggs; to the same cause is to be attributed the fact that silver spoons used in eating eggs are stained, silver sulphide being formed.

438. Fibrin is the name of a substance which separates in the solid state when fresh blood coagulates, either on standing, or on being beaten and stirred with twigs. The coloring matter of the blood may be removed, and the fibrin obtained, in the form of a white, stringy mass, by placing the clot on a fine sieve or cloth, and squeezing and washing it repeatedly with water. The composition of fibrin closely resembles that of albumin. The liquid substance in fresh blood, from which fibrin is derived, is called *fibrinogen*. A substance called *vegetable fibrin* occurs in gluten (§ 393). By washing a piece of lean meat in water, to remove the coloring matter, there will be obtained a substance which resembles fibrin in appearance, and was formerly called *flesh fibrin*. It is a mixture which consists chiefly of a substance known as *myosin*.

439. Casein occurs in the milk of animals. It bears some resemblance to albumin, but is not coagulated by heat. It is coagulated by acids and by rennet, the inner membrane of the stomach of the calf. Advantage is taken of this fact, in

the manufacture of cheese, which is made by warming the milk in contact with rennet: the casein is coagulated, and rises to the surface, carrying with it the fatty matters held suspended in the milk. The curd thus obtained, when pressed, and kept for some time, becomes cheese.

440. **Milk** consists mainly of water holding in solution casein, milk sugar, a little albumin, and certain salts, such as sodium and potassium chlorides, and the phosphates of calcium, magnesium, and the alkali metals. It holds in suspension a number of oily globules; and when allowed to stand quietly, these globules rise to the surface, forming the cream. The residue, after the removal of the cream and the coagulation of the casein, is the whey. Butter is made by agitating the cream, so as to break up the globules, and allow the fat to collect together in one mass.

Exp. 200. — Allow some fresh milk to stand until the cream has risen to the surface. Remove the cream by skimming, and to the skimmed milk add a little dilute sulphuric acid. The milk is *curdled*; that is, the casein is coagulated, and rises to the surface.

441. **Legumin** is a substance which resembles casein: it occurs in peas, beans, etc. The Chinese make a sort of vegetable cheese from peas.

442. **Gelatin and Glue.** — There is contained in the skin and bones of animals an insoluble substance known as *collagen*, — that in bones is often called *ossein*, — which, by long-continued boiling in water, changes to a substance readily soluble in hot water, which gelatinizes on cooling, and is known as *gelatin* or *glue*. Though allied in some sort to albumin, these substances differ from it in chemical composition, and they have much less nutritive value. Isinglass, as made from the swimming bladders of fishes, is nearly pure gelatin. A substance called *chitin*, which occurs in the skins of earthworms, etc., and in the shells of lobsters and crabs, is analogous in some respects to ossein.

Exp. 201. — Immerse a *clean* bone in dilute hydrochloric acid (made by diluting the commercial acid with six times its bulk of water). The mineral part of the bone will gradually dissolve away, and after three or four days there will be left a flexible substance

which preserves the shape of the bone, and, when dry, has a translucent, horny appearance. This is ossein.

Exp. 202.—Boil the ossein of Exp. 201 with water for several hours. It dissolves almost entirely, being converted into gelatin. Allow the concentrated solution to cool: it will gelatinize.

443. **Pepsin** is a substance obtainable from the inner coating of the stomachs of animals. It is an unorganized ferment akin to diastase (§ 387), and when in the presence of free acids, such as dilute hydrochloric acid, helps the latter to dissolve and change albumin, and most of the other nitrogenous constituents of foods, to such an extent that the new matters can pass from the alimentary canal into the so-called circulatory system of the body. **Trypsin** is another unorganized ferment found within the bodies of animals, in the so-called pancreatic juice. Unlike pepsin, it acts best in alkaline solutions. It does not act in the presence of acids. One of the most efficient of these unorganized digestive ferments is **papain**, obtained from the juice of the papaw tree. It is often prescribed by physicians as an aid to digestion, and also for removing false membranes, such as those which form in croup and diphtheria.

444. **Glycogen** ($C_6H_{10}O_5$)_n is a remarkable substance which has the same percentage composition as starch. It abounds in the livers of animals, and exists in small quantity in blood also, and in muscular fiber, as well as in fungi and some other plants. It can be obtained as a white powder by mincing fresh liver, boiling the fine meat in a weak solution of caustic potash, filtering, and adding alcohol to the filtrate. Like starch, glycogen can readily be converted into a sugar. The sweet taste of liver is due to the sugar formed from glycogen. If a bit of raw liver be washed with water until it is tasteless, and then left at rest, it will soon acquire a sweet taste. Experiments have shown that harm results if more than a small amount of sugar is introduced all at once into the veins of an animal; and it would appear that the liver acts to change the sugar, etc., of the food to glycogen, to hold this glycogen in store, and to dole out sugar from it into the blood constantly, though little by little. When boiled with dilute sulphuric acid, glycogen changes readily to dextrose.

445. **Decay of Organic Matter.**—Most organic substances are liable to undergo change, especially those which contain nitrogen. The fact is familiar to us through the speedy decay of dead animals and plants, unless, indeed, they have been dried or otherwise preserved. The ultimate or final products of the decay of animal or vegetable matter are mainly carbon dioxide and water, since the greater part of all organic matter is made up of carbon, hydrogen, and oxygen. This complete conversion

may take place rapidly when the substances are exposed to a high temperature, with free access of oxygen; but as a general rule, decay is slow, and is accompanied with the formation of a great variety of intermediate products, some of which are very offensive, especially when sulphur is an ingredient of the decaying substance. By the rapid decay of substances containing nitrogen, ammonia is formed. But nitrates are produced later, after putrefaction has run its course, and the well-rotted materials have come under the influence of the nitric ferments (§ 476).

Like those exhibited in fermentation (§ 387), the phenomena of decay and putrefaction are due to the presence of microscopic organisms. In other words, organic matters, at all stages of their decay, are subject to the attacks of a great variety of extremely minute organisms, which, according to their kinds, may cause one or another form of fermentation, or putrefaction, or slow wasting away. One result of these fermentations is, that a vast number of incompletely oxidized substances are formed before the last terms of decay (carbon dioxide and water) are arrived at. Among these intermediate products, *humus*, or vegetable mold, may be mentioned.

To illustrate the complexity of the chemical changes which occur, even in those kinds of fermentations which seem to be comparatively simple, it may be said, with regard to the fermentation of glucose (Exp. 138, § 292), that, although the equation there given to represent the decomposition of the sugar really does express the main reaction which occurs, there are nevertheless formed, in greater or less amounts, several other bodies beside the carbon dioxide and the alcohol. It is well known, in fact, that lactic and succinic acids, glycerin, and a brown substance resembling caramel, are among the usual products of the alcoholic fermentation.

446. The natural decay to which dead organized bodies are prone may be arrested more or less completely by the use of certain chemical agents which repel or destroy the ferment organisms, or by the simple exclusion of air after any adhering organisms or germs have been destroyed by heat. Warmth and moisture are among the conditions favorable for the multiplication of the microorganisms which cause decomposition. In a cold climate, or in winter, animal substances may be kept for a much longer period than in summer, because most kinds of ferments cannot live or thrive at low temperatures.

Among the chemical substances used as *antiseptic* or *preservative agents*, are common salt, which is used in the curing of meat and fish; wood smoke, which owes its virtue to the creosote (§ 369) contained in it, and which is used in the smoking of hams, herring, and other articles of food; creosote itself and carbolic acid; and the dead oil of tar (§ 360), used in preserving timber.

All these things are *germicides*. In the process of canning meats and vegetables, the materials are heated to destroy all ferment organisms which may be attached to them; and the cans are then sealed, so that their contents are out of contact with the air. The domestic processes of pickling and preserving depend upon the use of acids in which the microorganisms cannot live, or of sirup strong enough to be obnoxious to them.

CHAPTER XX.

THE METALLIC ELEMENTS.

447. Classification of the Elements. — The elements thus far considered belong to the class known as the *nonmetals*, or *nonmetallic elements*. They are distinguished more or less clearly from metals by the facts that comparatively few of them exhibit any metallic luster; that they are mostly non-conductors or feeble conductors of heat and electricity; that they generally form gaseous compounds with hydrogen; and that their oxides, on reacting with water, form acids. We have now to study the class of bodies known as *metals*, which are characterized by the peculiar luster called *metallic*; by the ease with which they conduct heat and electricity; by the fact, that, by replacing the hydrogen of acids, they form salts, and that their oxygen compounds, by reacting with water, form bases. It is to be understood, however, that no sharp line of distinction can be drawn between metals and nonmetals; for several elements possess the general characteristics of both these classes. Thus antimony has a metallic luster, and one

of its oxides acts as a base; while the fact that it forms a gaseous compound with hydrogen, and has oxides of acid character, would naturally place it among nonmetals. Bismuth also exhibits some nonmetallic characteristics to a marked degree, and is, on this account, often regarded as a nonmetal, although, if it were not for its chemical relationship to the other members of the nitrogen group, it would unquestionably always be classed with the metals. There are other elements, ordinarily regarded as metals, which occasionally play the part of nonmetals; and it may be said in general terms, that, while the division of the elements into metals and nonmetals is not wholly devoid of convenience, it is arbitrary, and no longer possesses the importance which was at one time attached to it.

It has been shown in previous chapters that the elements thus far studied fall into several natural groups or families, and that the members of each of these groups exhibit very similar properties. We have, in fact, considered most of the nonmetallic elements, in accordance with this natural classification, as members of one of the following groups:—

| CHLORINE GROUP. | SULPHUR GROUP. | NITROGEN GROUP. | CARBON GROUP. |
|-----------------|----------------|-----------------|---------------|
| (Halogens.) | Oxygen | Nitrogen | Boron |
| Fluorine | Sulphur | Phosphorus | Carbon |
| Chlorine | Selenium | Arsenic | Silicon |
| Bromine | Tellurium | Antimony | |
| Iodine | | Bismuth | |

It is to be remarked that hydrogen is not specially related to any one of these groups. It would seem to belong properly to the class of metals, although it stands somewhat by itself, and exhibits both metallic and nonmetallic characteristics.

In proceeding to study the metallic or base-forming elements, it will be seen that they also may conveniently be arranged in distinct natural groups, or families, the several members of which have many common properties, and are closely related to one another in respect to the physical and chemical characters of their compounds. Thus we shall become acquainted, in due course, with the following groups.

1. Alkali Group : Sodium, potassium, and several rare metals.
 2. Calcium Group : Calcium, strontium, and barium.
 3. Magnesium Group : Magnesium, zinc, cadmium, and glucinum.
 4. Lead Group : Lead and thallium.
 5. Copper Group : Copper, mercury, and silver.
 6. Cerium Group : A number of rare metals, including cerium, scandium, etc.
 7. Aluminum Group : Aluminum, gallium, and indium.
 8. Iron Group : Manganese, iron, cobalt, nickel.
 9. Chromium Group : Chromium, tungsten, uranium, molybdenum.
 10. Tin Group : Tin, titanium, germanium, zirconium, and thorium.
 11. Gold, and the Platinum Group : Gold, platinum, osmium, and the other elements which are found together with platinum.
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THE ALKALI GROUP.

SODIUM, POTASSIUM, AMMONIUM, LITHIUM, RUBIDIUM, CESIUM.

CHAPTER XXI.

SODIUM (Na).—ATOMIC WEIGHT, 23.

448. This abundant element is chiefly found in nature in the state of chloride, nitrate, carbonate, borate, and silicate. The most abundant of its compounds is common salt, which is a compound of sodium and chlorine (**NaCl**). On account of the inexhaustible abundance of common salt, this substance constitutes the chief source from which all manufactured compounds of sodium are more or less directly derived ; one other natural sodium-containing mineral, however, deserves mention as a source of sodium compounds,—the mineral cryolite, a double fluoride of sodium and aluminum (§ 89).

449. **Sodium Chloride, or Common Salt (NaCl).**—This natural mineral is, when pure, a colorless, transparent, anhydrous stone, which crystallizes in cubes, dissolves readily in about three times its weight of cold water, and possesses a specific

gravity of 2.15, and an agreeable taste, which, because familiar, is the representative or type of that peculiar savor called *saline*. A saline taste means a taste suggestive of that of common salt; just as the phrase *saline substance* characterizes a very large class of bodies which resemble more or less in appearance and properties the longest and best known of all such substances, — common salt.

There are three sources of salt, — the beds of the native mineral, saline springs, and sea water. In all cases in which the salt is obtained from its solution in water, evaporation by fire, or by the heat of the sun in warm, sunny climates, is necessary. When pure enough, the rock salt is mined like any other ore; but when it is mixed with earth or other impurities, as it lies in its natural bed, the solubility of the sodium chloride in water is availed of to free the salt from its insoluble impurities, and to facilitate the lifting of it to the surface of the earth. Water is let in to the bed of salt, and allowed to remain there till it has become saturated; the brine is then pumped out and evaporated. Some natural brine springs contain so small a proportion of salt, that some cheaper mode of evaporation than by fire is essential to their profitable working. Such waters are concentrated by a process termed *graduation*. The brine is pumped up into a great cistern, from which it is allowed to trickle over fagots placed in wooden frames, and built up to a great height in long regular walls, which are set across the direction of the prevailing wind. The brine, thus diffused over a very large surface, is rapidly concentrated by the draught of air. By repeating the process a moderate number of times, a weak brine may be brought to a degree of concentration at which evaporation by fire may be employed. If the strong brine is boiled down rapidly, a fine-grained table salt is obtained; if it is slowly evaporated, a hard, coarsely crystallized salt is the product. The thick *mother liquor*, from which no more sodium chloride will crystallize, contains the more soluble salts of the original brine, such as calcium chloride, magnesium chloride and bromide, beside a large proportion of common salt which cannot be separated from the liquor. Such mother liquors are sometimes so rich in magnesium salts as to be advantageously worked for these substances, and they are also sometimes profitable sources of bromine. Considerable quantities of magnesium salts and of bromine have also been extracted from concentrated sea water, after all the available sodium chloride has been withdrawn. The salt of commerce generally contains a small proportion of magnesium chloride, which makes it slightly deliquescent and bitter.

Sodium chloride crystallizes in cubes; sometimes the small cubic crystals formed at the surface of a slowly cooling solution arrange

themselves in the shape of hollow, four-sided pyramids. When perfectly pure, salt is not hygroscopic; but when crystals of salt are heated, they crackle, because of mechanically inclosed water.

Exp. 203.—Dissolve 9 g. of fine salt in 25 cc. of water at the ordinary temperature. Add to the solution another gram of salt: it will not dissolve. Bring the solution to boiling: the added gram of salt will barely dissolve. Sodium chloride is scarcely more soluble in hot than in cold water, wherein it differs from the great majority of soluble salts. Evaporated brines deposit their salt with almost equal facility when hot and when cold, but the hot liquors will hold in solution a much larger proportion of the salts with which the sodium chloride is associated than the cold brines could retain. In the process of evaporation by fire, the associated magnesium, calcium, and sodium salts do not, therefore, crystallize with the common salt, but remain in the hot mother liquor.

450. The uses of common salt are manifold. It is a constituent of almost all kinds of food, and essential to the life of animals; and it exists, in small quantities, in almost every soil, and in all natural waters. The antiseptic quality of salt is applied to the preservation of fish, meat, and wood. Salt is extensively employed in glazing earthenware, its volatility at furnace heat combining with other qualities to fit it for this use. Immense quantities of salt are consumed in preparing sodium sulphate, from which, in turn, common soda (sodium carbonate) is made. Salt is also the source from which hydrochloric acid is usually derived (§ 80).

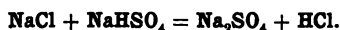
451. **Sodium sulphate** (Na_2SO_4) is made in great quantities from common salt and sulphuric acid, as a preliminary step in the manufacture of sodium carbonate.

The process has two stages. The mixture of salt and sulphuric acid is first heated in large, covered cast-iron pans. As in Exp. 41, § 80, hydrochloric acid is disengaged from the mixture, and is absorbed by being passed through vertical stone towers filled with lumps of coke, over which water is kept trickling. The reaction which takes place in the iron pans is not complete, a portion of the sodium chloride remaining undecomposed. The reaction at this first stage may be represented as follows:—



The pasty mass is then pushed into an adjoining fire-brick chamber, the floor of which rests upon a furnace flue. At the high tempera-

ture of this chamber, the sodium acid sulphate of the last reaction, known as *salt cake*, decomposes the remainder of the salt, and a further quantity of hydrochloric acid is disengaged, to be condensed by the water in the coke towers, while sodium sulphate remains, —

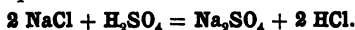


The sodium sulphate resulting from this process is a white, anhydrous salt, which dissolves easily in water at 30°. When a strong solution of the anhydrous salt, made at this temperature, is cooled, there separate large, colorless crystals of a transparent salt, bitter and cooling to the taste. This salt, long known as *Glauber's salt*, contains, beside the elements of sodium sulphate, ten molecules of water: it therefore answers to the formula $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$. The crystallized salt loses water on exposure to dry air; it *effloresces*, crumbling to a white powder, and is converted into the anhydrous salt.

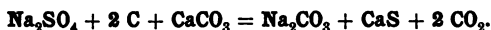
Exp. 204. — Dissolve 10 g. of crystallized Glauber's salt in water the temperature of which has been noted. During solution, the temperature falls. Cold is produced in consequence of the expenditure of some of the heat of the mixture in overcoming the cohesion of the crystallized salt. Mix a like quantity of the effloresced salt (anhydrous sodium sulphate) with a small bulk of water: heat will be developed. A part of the water is solidified by combining with the anhydrous sulphate to form the hydrated sulphate; and the heat, which before kept that quantity of water fluid, being set free to do other work, raises, by a certain amount, the temperature of the mixture.

452. Sodium Carbonate (Na_2CO_3). — The manufacture of this substance constitutes one of the most important branches of chemical industry. Immense quantities of it are consumed in the fabrication of glass and soap, in the preparation of the various compounds of sodium, and in washing, both by the manufacturer of cloth and in the household. The ashes of sea and seashore plants were formerly the source of the sodium carbonate; but it is now chiefly made from common salt by a process called, from the name of its French inventor, *Leblanc's process*.

The first stage of this process we have already studied. It consists in the preparation of the sodium sulphate from common salt by treatment with sulphuric acid: —



In the second stage, the sodium sulphate is mixed with coal and chalk, or limestone (calcium carbonate), and heated in a reverberatory furnace (Fig. 73). The carbon of the coal takes oxygen from the sodium sulphate (Na_2SO_4), and would leave sodium sulphide (Na_2S); but, at the same time, an interchange takes place between the sodium sulphide and the calcium carbonate, forming sodium carbonate and calcium sulphide. The conversion of the sulphate to carbonate may be expressed by the equation —



At the same time, some of the calcium carbonate is converted into calcium oxide. The chief products of the fusion are sodium carbonate and calcium sulphide and oxide, though, in addition to these substances, several other sulphur salts are present in small quantities.

The mass remaining after the reaction is complete is called *black ball* or *black ash*. When cold, it is systematically washed with warm water, until all the soluble portions are extracted. The solution is evaporated in large iron pans by the waste heat of the reverberatory furnaces, and again calcined. The product of this heating is the *soda ash* of commerce. It is almost white, and generally contains about 80 per cent of pure anhydrous sodium carbonate, together with some sodium hydroxide, sulphate, and chloride. As some caustic soda is always contained in the black ash, the solution is frequently concentrated until a hydrated carbonate crystallizes, of the composition $\text{Na}_2\text{CO}_3 \cdot 2 \text{H}_2\text{O}$, which is dipped out and dried, when it loses all its water. The mother liquor is used for the manufacture of caustic soda. The insoluble compound of calcium sulphide and oxide ($\text{CaO} \cdot 2 \text{CaS}$), left in the tanks in which "black ash" is leached, is known as *alkali waste*. Considerable quantities of sulphur are recovered from it nowadays.

Fig. 73 represents a reverberatory furnace such as is used in the manufacture of wrought iron. The furnaces used in the manufacture

of soda ash differ in their details from the one figured, but the general principle is the same. In a reverberatory furnace, the substance to be heated does not come into immediate contact with the fuel; the fire is built upon the grate bars (*G*), and the flame plays upon the hearth (*H*), the heat being reflected downward from the curved roof.

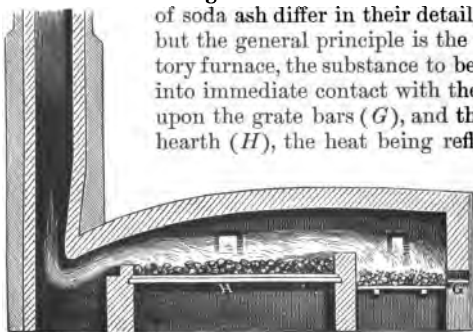


Fig. 73.

The so-called *crystals of soda*, or *washing soda*, are obtained by dissolving the crude soda ash in hot water, and suffer

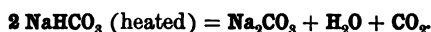
ing the hot solution to cool in large pans. In the course of five or six days, large, transparent crystals are formed, which contain 62.93 per cent of water, and correspond to the formula $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The crystals effloresce in the air. They have a disagreeable taste, called alkaline; are soluble in very large proportion, both in hot and cold water; and melt in part at a moderate temperature in their own water of crystallization. The crystals readily part with all their water, and the dry residue melts at a bright red heat. This residue is anhydrous sodium carbonate, purified by the process of crystallization which it has undergone. In this case, as in all others, the process of crystallization consists essentially in the aggregation of *like* particles. The strong tendency is to exclude heterogeneous particles, or, in other words, impurities, from the crystallizing structure. There is no more universally applicable and valuable means of purification than the process of crystallization. Another method of making sodium carbonate is described in § 454.

453. Sodium Acid Carbonate (NaHCO_3).— When masses of crystals of hydrated sodium carbonate (soda crystals) are exposed to an atmosphere of carbonic acid gas, they absorb carbon dioxide, with an evolution of heat sufficient to expel the greater part of their water of crystallization. The white powder thus obtained (NaHCO_3) is familiarly known as *bicarbonate of soda*. It is one of the ingredients in most of the artificial yeasts or baking powders used for raising bread, cake, and puddings, and is known to grocers and cooks as *soda*, or *baking soda*, although the constituent which is really utilized is the carbon dioxide.

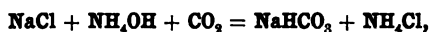
From sodium bicarbonate, carbonic acid may be set free by almost any acid or acid salt. Effervescing powders consist of sodium bicarbonate in one paper, and tartaric acid in another. On contact with water, carbonic acid is set free. If some sodium potassium tartrate be added to the contents of the first paper the laxative *Rochelle salt* will remain in the liquid (§ 417). When bread or cake is raised with soda and cream of tartar, the escaping carbon dioxide is the agent in puffing up the dough, and the same Rochelle salt remains in the bread. Tartaric acid and cream of tartar having been dear in late years, a cheaper baking powder has been made from calcium acid phosphate. When this substance reacts within the dough, with sodium bicarbonate, there remains in the bread a mixture of the phosphates of sodium and calcium. Alum has sometimes been used for the same purpose. Commercially speaking, it is most convenient to employ, in connection with the acid carbonate, either acids or acid salts, which

are solid, and not so corrosive as to be obviously dangerous or harmful; but in many cases hydrochloric acid may perfectly well be used, and in household economy it has long been customary to raise bread and cake with saleratus and sour milk, i.e., the lactic acid in the milk.

Sodium acid carbonate is much less soluble in water than the normal carbonate is: when heated, it gives up carbon dioxide and water, and is converted into the normal salt, —



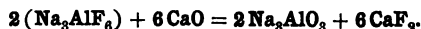
454. **The Ammonia-Soda Process.** — Large quantities of both the sodium carbonates are made nowadays by an ingenious process based on the reaction —



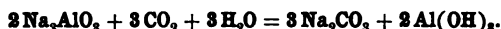
which depends on the difficult solubility of the sodium acid carbonate. It will have been repeatedly noticed already, that many reactions are determined by the fact, either that a volatile product may be formed when chemical substances are brought together, or an insoluble, or a difficultly soluble, product, as in the present instance. Numerous illustrations of these truths have already been given, as in the preparation of ammonia from ammonium chloride and lime (§ 77), and in the detection of carbon dioxide by means of limewater (Exp. 110, § 244).

To obtain the sodium carbonate, strong brine, saturated with ammonia gas, is placed in vertical cylinders, provided with many perforated shelves, and carbonic acid gas is forced into the liquid by means of a pump. Some heat is given off during the reaction, but the outside of the cylinders are cooled by means of a current of water. Sodium acid carbonate forms, and is deposited upon the shelves, in crusts. When the reaction is completed, the residual liquid, which contains some common salt and some ammonia, as well as ammonium chloride, is run off into stills, where it is treated with milk of lime, for making new charges of ammonia gas. By means of water and steam, the crusts on the shelves are dissolved, and, on cooling the solution, sodium acid carbonate crystallizes out. It may either be dried and sold as such, or converted into plain sodium carbonate by ignition. These products are much purer than those obtained by Leblanc's process; but there are cases when the older method has its advantages, as at those chemical works where large quantities of hydrochloric acid are required for making bleaching powder.

455. In this country a considerable quantity of soda is obtained from cryolite (Na_3AlF_6), which occurs in great deposits in Greenland. The pulverized mineral is heated with lime, when sodium aluminat and calcium fluoride are formed, —

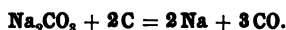


On treating the mass with water, the sodium aluminate will dissolve, while calcium fluoride remains unacted upon. On passing carbon dioxide through the filtered solution, sodium carbonate is formed, and remains dissolved, while aluminum hydroxide is precipitated, —



The sodium carbonate is obtained by evaporating the filtered solution, and the aluminum hydroxide may be used for preparing salts of aluminum, etc.

456. Sodium (Na). — The element sodium is never found uncombined in nature, for the reason that in its elementary condition it cannot exist in contact with either air or water. It may be prepared by heating sodium carbonate with carbon in an iron retort to a high temperature, —



The metal distills over, and is condensed in receivers, and the liquefied sodium is collected under petroleum. Another method consists in reducing sodium hydroxide by heating it with an intimate mixture of finely divided iron and carbon. Sodium is manufactured also nowadays by the electrolysis of the hydroxide. In this way it is obtained directly in the liquid, i.e. melted, condition.

The properties of the element sodium are very curious. The substance, when freshly cut, or when melted under naphtha, or in an atmosphere artificially deprived of oxygen, has the brilliant, white, metallic luster of silver. Though possessing so eminently this characteristic property of the class of bodies called metals, and being, like them, a good conductor of heat and electricity, sodium is far from resembling the ordinary metals in other respects. Thus it is lighter than water, having a specific gravity of only 0.973, whereas the common metals are dense and heavy; again, it is as soft as wax at common temperatures, and melts at a temperature below that of boiling water; while it has none of the comparative permanence which characterizes lead, tin, copper, silver, gold, and other familiar metals. If exposed to the air, even for a few seconds only, it tarnishes, being acted upon by the moisture in the air, and soon becomes covered with a coating

of hydroxide: hence the necessity of preserving the metal under some liquid which, like naphtha, contains no oxygen. We have already seen that sodium decomposes cold water (Exp. 8, § 26), setting free its hydrogen, and combining with its oxygen.

Exp. 205.—Cover the bottom of a large bottle (at least a liter bottle) with hot water, drop in a piece of sodium as large as a small pea, and immediately cover the mouth of the bottle with a card or glass plate. The heat caused by the chemical combination of the sodium and the oxygen of the water is sufficient to inflame the hydrogen set free. The escaping hydrogen carries with it a small portion of the volatilized sodium, and therefore burns with an intensely yellow flame, which is very characteristic of sodium compounds. The metal swims rapidly about on the surface of the water, and is completely converted into caustic soda. At a little interval, after the flame has ceased to burn, a globule of sodium hydroxide, which has escaped solution, bursts, and scatters in all directions. The mouth of the bottle should always be covered, to avoid the possible projection of particles of hot soda out of the bottle.

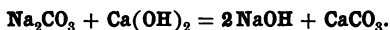


Fig. 74.

The water in the bottle, tested with litmus paper, will be found to possess a strong alkaline reaction. If the bit of sodium be previously wrapped up in a piece of cloth, it will take fire in cold water, or even on ice. The cloth prevents the sodium from moving about, and the heat of combination is therefore concentrated upon one spot.

Sodium is a powerful reducing agent, and is used for the isolation of some elements, such as magnesium and aluminum, whose oxides cannot easily be reduced. In combination with mercury as sodium amalgam, it is used in obtaining silver and gold from their ores.

457. Sodium Hydroxide (NaOH).—When sodium reacts with water, a solution of *sodium hydroxide*, possessing an intensely alkaline reaction, remains behind: the hydroxide is, in practice, made from the carbonate. The sodium carbonate is dissolved in boiling water, and slaked lime mixed with water to the consistency of cream is run into the hot liquor. The calcium of the slaked lime replaces the sodium in the sodium carbonate; a white, insoluble precipitate of calcium carbonate is formed; and sodium hydroxide remains in the solution:—



The solution of sodium hydroxide, after separation from the

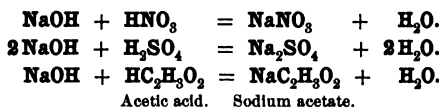
precipitate of calcium carbonate, is evaporated until it has come to the desired strength. The evaporation may be continued, until, at a nearly red heat, an oily liquid is obtained, which solidifies, on cooling, to a white, somewhat translucent mass, whose composition corresponds to the formula NaOH . It is very soluble in water, and rapidly absorbs both water and carbonic acid from the air.

458. **Caustic soda** is manufactured in large quantities, principally for the use of the soap maker. Soap, as we have already seen (Exp. 149, § 317), is made by boiling together grease or oil with caustic soda or potash. Soda lye yields a hard soap; potash lye, a soft soap.

The cleansing action of soap, on which its use depends, may be explained as follows. When soap is dissolved in water, it undergoes a chemical change: regarding the soap as sodium stearate, we may say that a partial interchange takes place between the sodium of the soap and the hydrogen of the water, and there is formed a sodium acid stearate and a certain amount of caustic soda. The caustic alkali thus set free attacks the greasy and oily matters of the article to be cleansed, and the somewhat sticky solution of soap holds in suspension, and thus removes mechanically the particles of dust and other insoluble matters.

459. Sodium hydroxide is an example of the class of bodies called *bases* (§ 67). It colors litmus blue, and turmeric brown; and, when it is mixed in due proportion with an acid, a saline compound is formed which is neither acid nor alkaline, and which may bear no more resemblance to its proximate constituents than bread bears to flour and water, or rust to iron and oxygen.

From such reactions between acids and sodium hydroxide, water is always disengaged simultaneously with the saline product, as may be illustrated by the following examples (compare also §§ 67-69):—



Acetic acid. Sodium acetate.

While recognizing the frequent occurrence of such reactions as are thus represented between hydroxides, it must not be forgotten that many anhydrous saline compounds can be made by the direct combination, under appropriate conditions, of two oxides which contain no hydrogen. By heating one molecule of sodium hydroxide, or 40 parts, by weight, with one molecule, or 23 parts, by weight, of sodium, an

oxide of sodium (Na_2O) is obtained, which contains no hydrogen; but this body has none of the properties described by the adjective *alkaline*, any more than the anhydrous trioxide of sulphur possesses the properties suggested to the mind by the term *acid*. Now, the very same sodium sulphate which results from the second of the above reactions, may be prepared by bringing together this sodium oxide and sulphuric anhydride, —



There exists another anhydrous oxide of sodium, corresponding in composition to the formula Na_2O_2 , and the same sodium sulphate can be made by heating this oxide with sulphurous anhydride, —



These facts show that a knowledge of the substances from which a salt may be made is not sufficient to establish any presumption concerning the molecular constitution of the salt itself.

460. **Sodium Diborate, or Borax** ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$). — *Borax* is a colorless, crystalline salt, occurring ready formed in nature. It is found incrusting the soil of certain marshes in California, and in several localities in Asia. Considerable quantities are made artificially from a mineral, calcium borate, and some is prepared from the native boracic acid of Tuscany (§ 222) by the addition of sodium carbonate. Carbon dioxide is set free, and the borax crystallizes out from the solution.

Borax has a feebly alkaline taste and reaction. When heated, it bubbles up, loses its water, and melts below redness, into a transparent glass. This glass dissolves many oxides of the metals, acquiring thereby various colors characteristic of these oxides: hence borax is much used as a blowpipe test for determining the presence of certain oxides from the metals.


Exp. 206. — Make a little loop, about as large as this  on the end of a bit of fine platinum wire 6 or 8 cm. long. Heat the loop white-hot in the blowpipe flame, and thrust it, while hot, into some powdered borax: a quantity of borax will adhere to the hot wire. Reheat the loop in the oxidizing flame: the borax will puff up at first, and then fuse to a transparent glass. If enough borax to form a solid, transparent bead within the loop does not adhere to the hot wire the first time, the hot loop may be dipped a second time into the powdered borax. When a transparent

Fig. 75.

glass has been formed within the loop of the platinum wire, touch the bead of glass, while it is hot and soft, to a speck of manganese dioxide no bigger than the period of this type. Reheat the bead with the adhering particle of oxide in the oxidizing flame: the black speck will gradually dissolve, and, on looking through the bead towards the light, or a white wall, when the oxide has disappeared, the glass will be seen to have assumed a purplish red color.

The same experiment may be performed with iron oxide, which imparts to the glass a yellow color; or with copper oxide, which imparts a bluish green color. The oxidizing flame must be used in both these cases, as with the manganese oxide.

The power which borax possesses, of dissolving metallic oxides, suggests an explanation of its use in brazing and in soldering the precious metals. The solder will only adhere to a bright and clean metallic surface, and the borax which melts with the solder removes from the pieces of metal the film of oxide, which would otherwise prevent the adhesion of the solder. Borax is also used by the assayer and refiner as a flux; in medicine; and as an antiseptic agent.

461. Other Compounds of Sodium. — Sodium nitrate (NaNO_3), a somewhat deliquescent and very soluble salt, occurs abundantly on the surface of the soil in certain desert districts of Chile. It is employed in the manufacture of nitric and sulphuric acids, and as a fertilizer. There are several phosphates of sodium corresponding to the different varieties of phosphoric acid. The most familiar of these phosphates, and the one commonly called *sodium phosphate*, is a crystallized salt of the formula $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$.

462. Sodium Sulphide. — Compounds of sodium and sulphur may be formed by heating sodium sulphate (Na_2SO_4) with charcoal, by heating sodium carbonate and sulphur together, and by boiling sulphur with caustic soda. There are five different compounds (Na_2S , Na_2S_2 , Na_2S_3 , Na_2S_4 , Na_2S_5), all soluble in water. When treated with an acid, they all give off hydrogen sulphide (§ 136), and from all except the first there falls a precipitate of finely divided sulphur, known as *milk of sulphur*. There is also a compound (NaSH), called *sodium hydrosulphide*, analogous in composition to sodium hydroxide (NaOH).

Exp. 307. — Into a small flask put a pinch of flowers of sulphur and two teaspoonfuls of a solution of caustic soda. Boil the solution for some minutes: the sulphur disappears, and the liquid becomes dark-colored. To the solution of sodium sulphide thus obtained, add dilute hydrochloric acid until the mixture turns litmus paper red; observe the odor of hydrogen sulphide, and also the precipitate of sulphur.



Fig. 76.

463. Sodium silicates may be prepared by dissolving silica in caustic soda, or by fusing together silica and sodium carbonate. The silicate of commerce, called *water glass*, is of varying composition. Sodium silicate is an ingredient of common glass, as has already been seen.

Sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), commonly called *hypo-sulphite of soda*, is a crystallized salt much used by photographers, because its aqueous solution is capable of dissolving silver chloride, bromide, and iodide, — compounds much employed by the photographer, and very insoluble in water.

CHAPTER XXII.

POTASSIUM (K). — ATOMIC WEIGHT, 39.

464. Until a comparatively recent period, **potassium** compounds were obtained chiefly from the ashes of plants; and *potassium hydroxide*, or *potash* (§ 467), was long known as the *vegetable alkali*. Plants have need of potassium, in order that they may grow; and they are able to collect from the soil and to assimilate potassium compounds, which can be recovered from the ashes that are left when the plants are burned. By leaching the ashes with water, and evaporating the filtrate to dryness, *potashes* are obtained; and *pearlash* is made by refining the crude potashes.

Exp. 208. — Place a handful of wood ashes on a filter, and pour hot water over them, collecting the filtrate in a bottle, and returning it

upon the ashes two or three times, in order to obtain a stronger solution. If the intention were to exhaust the ashes, they would have to be treated with several successive portions of mere water. The solution will be found to have a strongly alkaline reaction. A few drops of it, poured into a test tube containing a little dilute acid, occasion a brisk effervescence, a reaction from which we readily surmise the truth, that the potassium salt contained in the solution is *potassium carbonate*. By evaporating the rest of the solution to dryness in a porcelain dish, we obtain a small sample of crude potashes.



Fig. 77.

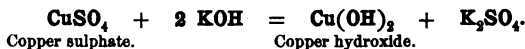
465. Potassium carbonate (K_2CO_3) is a hygroscopic and very soluble salt. When exposed to damp air, it becomes moist, and finally deliquesces. In this respect, it does not resemble soda ash, which is not hygroscopic, and is, for this reason among others, better adapted than potash for transportation and storing, and for most commercial uses.

Formerly potassium carbonate was the most important source of alkali, but it was put in the background when Leblanc's process made soda cheaper than potash. Latterly potash has again come to the front in some measure, since it has been made very cheaply at Stassfurt from potassium chloride. It has always been largely used in the manufacture of soft soap and the better kinds of glass. Potassium hydroxide (caustic potash) is made from it and many other compounds of potassium.

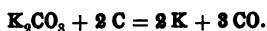
466. Potassium Acid Carbonate ($KHCO_3$).—This salt, commonly called *bicarbonate of potash*, may be prepared by passing a current of carbon dioxide through a strong solution of potassium carbonate: crystals of the bicarbonate will be deposited, which are permanent in the air. Saleratus is properly potassium bicarbonate, but sodium bicarbonate is often substituted for it.

467. Potassium Hydroxide (KOH).—The manufacture of potassium hydroxide, commonly called *caustic potash*, from potassium carbonate, resembles in every detail the preparation of caustic soda from sodium carbonate (§ 457). Potassium hydroxide is a hard, whitish substance, possessing a peculiar odor and a very acrid taste. Like sodium hydroxide, it rapidly absorbs moisture and carbonic acid from the air; and, since the potassium carbonate thus formed is a deliquescent salt, this change will go on until the entire mass of the hydroxide is converted into a sirup of the carbonate, whereas in the case of sodium hydroxide the absorption of water and carbonic acid is soon arrested by the formation of a coating of nondeliquescent sodium carbonate upon the surface of the lump of hydroxide. Potassium hydroxide is the strongest of the bases: it decomposes the salts of most other metals. Cast into small sticks, it is employed by physicians as a cautery, — a use which illustrates forcibly its destructive effect upon animal and vegetable matters. Like sodium hydroxide, its solution destroys ordinary paper, and cannot be filtered except through some refractory substance, such as asbestos or guncotton. A clear solution is best obtained by decantation from off the subsided impurities. In the laboratory, solutions of caustic potash and caustic soda are in frequent use for absorbing acid gases, such as carbon dioxide, and especially for separating the hydroxides of other metals from solutions of their salts.

Exp. 209. — Dissolve a crystal of blue vitriol (copper sulphate) in a few cubic centimeters of cold water, and add to the solution several drops of a solution of caustic potash. Copper hydroxide is thrown down as a delicate, blue, insoluble precipitate, while colorless potassium sulphate remains in solution: —



468. Potassium, like sodium, is made from its carbonate by heating intensely a mixture of the carbonate and charcoal in accordance with the reaction —



Potassium is a silver-white substance, of very brilliant luster, which is brittle at 0°, soft as wax at ordinary temperatures,

fuses at $62^{\circ}.5$, and is volatile below red heat, yielding a green vapor. It is lighter than water, having a specific gravity of only 0.865. It is almost instantaneously oxidized by air and water at the ordinary temperature, and, when heated, by nearly every gas or liquid which contains oxygen. Like sodium, it must therefore be collected and kept under naphtha, out of contact with the air.

Exp. 210. — Throw a piece of potassium, as large as a small pea upon some cold water in the bottom of a large bottle, and place a card or glass plate over the mouth of the bottle. The potassium decomposes the water, heat evolves enough to kindle the hydrogen which is given off. This hydrogen burns with a purplish red color, imparted to the flame by a minute quantity of vaporized potassium. This color is characteristic of potassium compounds, as a yellow color is characteristic of sodium compounds. The water will have an alkaline reaction from the formation of potassium hydroxide.

Exp. 211. — To a gas bottle in which carbonic acid is being steadily evolved (according to Exp. 112, § 245) attach a chloride-of-calcium tube; and beyond this drying tube, a short tube of hard glass, from which an exit tube leads into a small open bottle, as shown in Fig. 79. When the extinction of a lighted match in the open bottle proves the apparatus to be full of the carbon dioxide, thrust into the hard-glass tube a bit of potassium as big as a pea, previously dried



Fig. 78.

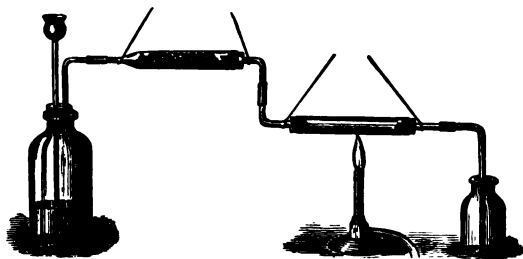
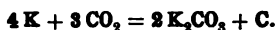


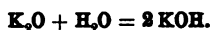
Fig. 79.

between folds of blotting paper, and gently heat the potassium with a lamp. The potassium will take fire, and burn at the expense of the oxygen of the carbon dioxide, and black particles of carbon will be deposited upon the walls of the tube. After the reaction has ceased, and the tube has been allowed to become cold, place it in a bottle of

water, so that the saline mass (potassium carbonate) may dissolve; the particles of carbon will then be seen more clearly, floating in the liquid. They may be collected upon a filter. The reaction which has taken place may be thus expressed:—



469. **Potassium oxide (K_2O)** can be obtained by burning potassium in the air, and heating the residue to a high temperature. With water it unites, with the evolution of heat, to form the hydroxide,—



Potassium also forms other oxides.

470. **Potassium chloride (KCl)** is an important source of potassium compounds, and is much used as a fertilizer. It occurs in sea water and in brine springs; it occurs also with other minerals in extensive deposits near Stassfurt in Germany, whence vast quantities of potassium compounds are extracted, and sent over the world. It resembles common salt in appearance and in taste, though it is somewhat more soluble in water, and volatilizes at a lower temperature.

Potassium bromide (KBr) and **iodide (KI)** resemble the chloride. All these salts are soluble, and they crystallize in cubes. They are much used in medicine, and the iodide is extensively employed by photographers.

471. **Potassium cyanide (KCN)** is a white, fusible, deliquescent solid, which may be made by fusing nitrogenous organic matter with potassium carbonate or hydroxide. It is of great use in galvanic gilding and silvering, since gold and silver cyanides are both soluble in a solution of potassium cyanide, with formation of double cyanides: thus silver cyanide forms the compound AgCy KCy , or AgKCy_2 . In the double cyanides, which potassium cyanide forms by uniting with the cyanides of certain other metallic elements, the cyanogen group is usually represented by the symbol Cy , as in the formulas here printed. A solution of potassium cyanide dissolves silver sulphide, and has therefore been suggested for household use in cleaning silverware. Photographers sometimes use it for removing stains of silver nitrate from the hands; but both

these applications of potassium cyanide are dangerous and inexpedient, for the cyanide is intensely poisonous, not only when taken internally, but also when brought in contact with an abrasion of the skin, a cut, or scratch. As a reducing agent, potassium cyanide has great power; it is especially useful in blowpipe reactions.



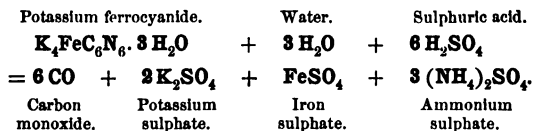
Fig. 80.

Exp. 212. — Scoop out a little hollow near one end of a bit of charcoal 8 to 12 cm. long. Introduce into the hollow a mixture of equal parts of tin oxide (SnO_2), dry sodium carbonate, and potassium cyanide. Heat with the reducing blowpipe flame for a minute or two. Metallic tin will be reduced, —



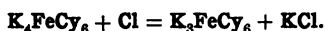
472. Potassium Ferrocyanide (K_4FeCy_6). — When potassium carbonate is fused with nitrogenous organic matter, potassium cyanide is formed, as has been stated in the preceding section. When this fusion takes place in the presence of iron (as iron filings, for instance), the fused mass treated with water yields a solution of a salt known as *potassium ferrocyanide*. This salt crystallizes in large yellow crystals, and is met with in commerce, under the name of *yellow prussiate of potash*, nearly in a state of purity.

Potassium ferrocyanide is a salt of an acid called *ferrohydrocyanic acid* (H_4FeCy_6), a compound of hydrogen with the hypothetical quadrivalent radical *ferrocyanogen* (FeCy_6 or Fcy). When potassium ferrocyanide is heated with sulphuric acid, it is decomposed in accordance with the reaction —



This reaction has already been taken advantage of in the preparation of carbon monoxide (Exp. 119, § 252).

473. Potassium Ferricyanide (K_3FeCy_6).— When a current of chlorine gas is passed through a solution of ferrocyanide of potassium, the following reaction takes place:—



The compound K_3FeCy_6 (potassium ferricyanide) may be obtained in beautiful deep red crystals by evaporating the solution. This compound is known in commerce as *red prussiate of potash*.

Potassium ferricyanide is a salt of ferrihydrocyanic acid (H_3FeCy_6), a compound of hydrogen with the hypothetical trivalent radical $FeCy_6$. The ferro- and ferri-cyanides of potassium afford valuable means of identifying iron in its compounds, as will be seen in § 600.

474. Potassium sulphate (K_2SO_4) differs from sodium sulphate in crystallizing as an anhydrous salt. It is a valued fertilizer, and large quantities of it are prepared at Stassfurt. It enters into the composition of many of the double sulphates, which are called *alums*, from the name of the commonest member of the class, the aluminum and potassium sulphate.

475. Potassium Acid Sulphate ($KHSO_4$).— This salt, commonly called the *bisulphate*, is formed on a large scale as a residuary product, admixed with the normal sulphate whenever nitric acid is manufactured from potassium nitrate, or hydrochloric acid from potassium chloride. When ignited, sulphuric acid is given off, and potassium sulphate remains, —



476. Potassium Nitrate (KNO_3).— This valuable salt, commonly called *saltpeter*, or *niter*, is very widely diffused in nature. In many localities it is found in caverns or caves in calcareous formations; but the chief commercial source of the salt is the soil of tropical regions, especially of certain districts in India, where the nitrate is found, in the dry season, as an efflorescence upon the surface of the ground, or in the upper portion of the soil itself. The saltpeter is extracted by treating the earth with water, and obtained in an impure state by evaporating the solution. The crude product is purified by successive recrystallizations.

This natural production of nitrates depends on the presence of certain microscopic organisms, which, when living under fit conditions in respect to warmth, moisture, air, and a slight degree of alkalinity, can respectively change ammonium salts to nitrites, and nitrites to nitrates. Thanks to the activity of these microorganisms, nitrates are seldom absent from fertile soils, or from spring or river water. The well waters of towns often contain large quantities of nitrates, from having been contaminated with matters from sewers or cess-pools. The presence in a soil, of thoroughly well-rotted manure, is favorable for the process of *nitrification*; but no nitrates form when animal or vegetable matters are actually putrefying or undergoing hot fermentation. The ferments which cause nitrification are easily killed by many kinds of chemicals, such as strong saline solutions, which act towards them as poisons.

477. Potassium nitrate is white, inodorous, and anhydrous, and has a cooling, bitter taste. When pure, it is permanent in the air, — a fact of great importance, inasmuch as the chief use of this salt is in the manufacture of gunpowder. Were it hygroscopic, like sodium nitrate, it would not be so readily applicable to this use. It is very soluble in water, especially in hot water. It melts, below a red heat, to a colorless liquid, without loss of substance; but at a red heat, it gives off oxygen, and suffers decomposition. Its most marked chemical characteristic is its oxidizing power.

Exp. 213. — Mix 5 g. of powdered saltpeter with 1 g. of dry, powdered charcoal; place the mixture on a piece of porcelain, and ignite it with a hot wire. When the deflagration is over, a white solid will be found upon the porcelain. Dissolve this solid in a few drops of water: the solution will be alkaline to test paper. Add a few drops of a dilute acid: a brisk effervescence marks the escape of carbonic acid. The nitrate has oxidized the carbon to carbon dioxide, part of which escaped with the nitrogen during the deflagration, while part entered into combination with the potassium, —



Fig. 81.



Gunpowder is an intimate mechanical mixture of soft-wood charcoal, sulphur, and potassium nitrate, in the proportions of 70 or 80 per cent of the nitrate, to 10 or 12 per cent of each of the other ingredients.

When gunpowder burns in a closed space, the reaction that takes place is quite complex. Speaking in general terms, however, we may say that the oxygen of the nitrate combines with the carbon to form carbon dioxide and carbon monoxide, while the sulphur is largely retained by the potassium, and nitrogen is left free. A very large proportion of gas, as compared with the bulk of the solid powder, is thus evolved when powder is burned. Moreover, gunpowder burns rapidly, and with great evolution of heat; so that the volume of gas, large at any temperature, is enormously expanded at the moment of its formation: hence it happens that the gas set free may be capable of occupying a thousand or fifteen hundred times as much space as the powder which generated it. An enormous pressure is thus engendered at the spot where the powder burns, and to this pressure some part of the matter which confines the powder must yield. In the case of firearms, it is the ball which yields to the pressure; in blasting, it is the solid rock itself that is torn apart.

478. **Potassium chlorate** (KClO_3) is a white, crystallized salt much used in medicine, in calico printing, in pyrotechny, in the manufacture of matches, and in the chemical laboratory, on account of its large oxygen contents. It is an oxidizing agent of the most vigorous description. At a red heat it is resolved into potassium chloride and oxygen (Exp. 4, § 12),—



Potassium chlorate is so prompt an oxidizing agent, that mixtures of it with combustible bodies often detonate violently when struck or heated. These combustions are attended with great danger, unless very small quantities be used.

Exp. 214.—Provide a bit of ordinary phosphorus as large as a pin's head; add enough finely powdered potassium chlorate to cover the phosphorus; fold the mixture tightly in a small piece of writing paper; place the parcel upon an anvil, and strike it sharply with a hammer. The mixture will explode with violence.

Strong acids, like sulphuric, nitric, and hydrochloric acids, decompose potassium chlorate, with evolution of oxides of chlorine, or of chlorine and oxygen. The decomposition is often attended with decrepitation, and sometimes with a flashing light. Combustibles, like sulphur, phosphorus, sugar, and resin, are inflamed by the gases evolved, as has been shown in Exp. 51, § 100.

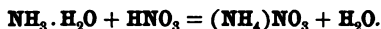
Exp. 215. — Rub 4 or 5 g. of clean potassium chlorate, free from dust, to a fine powder in a porcelain mortar. In powdering potassium chlorate, care must be taken that the mortar and pestle are perfectly clean, and that the salt is free from organic matter. Violent percussion and heavy pressure upon the contents of the mortar must be wholly avoided. Place the powdered chlorate on a piece of paper; add an equal bulk of dry, powdered sugar to the pile; and, with the fingers and a piece of card, mix the two materials thoroughly together. Mixtures of potassium chlorate and organic matter are liable to explode, if strongly rubbed or but lightly struck. Wrap the mixture in a paper cylinder, and place the cylinder on a brick in a strong draught of air. Let fall upon the mixture a drop of sulphuric acid from the end of a glass rod: a very vivid combustion will ensue, with the violet-colored flame characteristic of potassium.

479. **Potassium tartrate** ($\text{K}_2\text{C}_4\text{H}_4\text{O}_6$) is a very soluble crystalline salt. The potassium acid tartrate ($\text{KHC}_4\text{H}_4\text{O}_6$), known in the crude state as *argol*, and when purified as *cream of tartar*, has already been described in § 416.

CHAPTER XXIII.

AMMONIUM SALTS.

480. By neutralizing an aqueous solution of ammonia with nitric acid, there is formed a substance, $(\text{NH}_4)\text{NO}_3$, with which we are already familiar (Exp. 24, § 50), in accordance with a reaction which may be written —

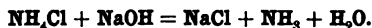


This substance corresponds in composition to potassium nitrate (KNO_3), except that the group of atoms NH_4 takes the place of the atom K . If we had used hydrochloric acid, there would have been formed a body (NH_4Cl) corresponding to potassium chloride (KCl). Sulphuric acid would give $(\text{NH}_4)_2\text{SO}_4$, corresponding to K_2SO_4 . To explain the constitution of these and similar salts, the group of atoms NH_4 is regarded as playing the part of a metallic element, like sodium or potassium, and has

received the name *ammonium*. We have, however, no positive evidence of the separate existence and metallic character of this group of atoms, NH_4 .

All ammonium salts, whether solid or in solution, evolve ammonia gas (NH_3) when heated with the hydroxides of sodium, potassium, calcium, and a few other metals.

Exp. 216. — To a few cubic centimeters of a solution of ammonium chloride in a test tube, add a few drops of a solution of caustic soda, and boil the liquid. The gaseous ammonia can be detected by its odor. If in any case the ammonia evolved be in so small a quantity that its characteristic smell cannot be detected, it may be recognized by its property of restoring the blue color to reddened litmus paper (§ 65), and of forming white fumes by contact with a rod moistened with somewhat dilute hydrochloric acid. The reaction may be formulated as follows:—



481. The solution of ammonia gas in water ($\text{NH}_3 \cdot \text{H}_2\text{O}$) may be regarded as a solution of ammonium hydroxide ($(\text{NH}_4)\text{OH}$) comparable with the solution of sodium hydroxide (NaOH) or of potassium hydroxide (KOH). It neutralizes acids, and forms emulsions with fats (§ 320), and is, indeed, often spoken of as *caustic ammonia*. It is, in short, a powerful base, capable of producing many of the effects which solutions of the fixed alkalies produce. To distinguish it from these last, ammonia was formerly called *the volatile alkali*. Ammonia water is much used in the analytical laboratory for neutralizing acids, and particularly for separating the hydroxides of metals from solutions of their salts.

Exp. 217. — Dissolve a small crystal of alum in 6 to 8 cc. of water in a test tube, and add ammonia water until the solution, after being well shaken, smells strongly of ammonia. A gelatinous precipitate of aluminum hydroxide will appear in the liquid.

Ammonium salts are very numerous, but only the few which are of present importance in the useful arts will be here described.

482. **Ammonium Chloride** (NH_4Cl).—This salt, commonly called *sal ammoniac*, is found native in many volcanic regions.

In the beginning, the commercial supply of this salt was obtained from the soot resulting from the incomplete combustion of camels'

dung; but nowadays the raw material, whence ammonium salts are manufactured, is chiefly derived from gas works and boneblack factories. Coal and bones contain a portion of nitrogen, which, during the process of distillation, is partially converted into ammonia (§ 76). This ammonia combines with the carbonic acid and hydrogen sulphide, which are likewise products of the distillation; and these compounds are condensed into a somewhat watery liquor, contaminated with tarry and oily matters, from which the ammonium salts are subsequently extracted.

Ammonium chloride serves for the preparation of ammonia (Exp. 39, § 77) and of ammonium carbonate. It is somewhat employed in dyeing, and also in certain processes with metals, such as tinning, soldering, and silvering copper and brass, and galvanizing (zincing) iron. When heated, it sublimes much below redness, without undergoing fusion. At the same time, a dissociation into NH_3 and HCl takes place; but the products combine again, on cooling, to form ammonium chloride.

Exp. 218. — Heat a small bit of sal ammoniac on a piece of porcelain, and observe the low temperature at which the solid is completely converted into vapor.

483. Ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) is a colorless, crystalline salt resembling potassium sulphate. It is employed in the manufacture of ammonium alum, as a fertilizer, and as a source of other ammonium salts.

484. Ammonium Nitrate ($(\text{NH}_4)\text{NO}_3$). — The method of preparing this salt, and its complete decomposition by heat, have already been described (Exp. 24, § 50; § 75). The salt crystallizes in long needles, which are somewhat hygroscopic. It has a pungent taste, is very soluble in water, and, in dissolving, produces sharp cold.

485. Ammonium Carbonates. — The commercial carbonate (*sal volatile*) is a white, semitransparent, fibrous substance, with a pungent taste and a strong ammoniacal smell. It is obtained by the dry distillation of bones, horn, and other animal matters; and the product may be purified from empyreumatic substances by repeated sublimation. Ammonium carbonate is obtained also by heating the chloride (or sulphate) with calcium carbonate: the ammonium carbonate sublimes, leaving a

residue of calcium chloride (or sulphate). There are several ammonium carbonates: the most permanent is the *bicarbonate*, or *ammonium acid carbonate* ($\text{NH}_4\cdot\text{HCO}_3$). The commercial carbonate gradually changes to bicarbonate in the air, where the more volatile neutral carbonate escapes.

486. The **sulphides** of ammonium correspond to those of sodium (§ 462). A solution of the sulphide ($(\text{NH}_4)_2\text{S}$), which is colorless when fresh, but gradually becomes yellow, owing to the formation of higher sulphides, is much used in the analytical laboratory.

487. A double phosphate of sodium and ammonium ($\text{NH}_4\text{NaHPO}_4\cdot 4\text{H}_2\text{O}$), known as *microcosmic salt*, is frequently used in blowpipe experiments.

488. **Isomorphism.** — The resemblance of salts of ammonium to those of potassium of the same name is the more striking from the fact that—as in many other cases of corresponding salts—their crystalline form, as well as their texture, color, and luster, are identical. If solutions of the two salts were mixed, it would be difficult subsequently to separate either one of the salts by itself, by way of crystallization; for, on evaporating the solution, there would be obtained crystals composed of the two salts mixed in the most varied proportions. Bodies which are thus capable of crystallizing together in all proportions, without alteration of the crystalline form, are said to be *isomorphous*, “like formed” (§ 576).

CHAPTER XXIV.

LITHIUM, RUBIDIUM, AND CESIUM.

SPECTRUM ANALYSIS.

489. **Lithium (Li).** — This rare metal occurs as a constituent of not a few minerals, especially micas and feldspars, but does not form a large percentage of any of them. In very small proportion, it has been recognized in sea water, mineral waters, and almost all spring waters, in milk, tobacco and other plants,

and in human blood. It is a widely diffused, but not abundant substance.

Metallic lithium resembles sodium and potassium in appearance and in its chemical relations. It is the lightest of all known solids which include no air, its specific gravity being only 0.59. The atomic weight of the element is also low; namely, 7.

All volatile lithium compounds color the flame of gas, alcohol, or the blowpipe carmine-red. The most delicate reaction for the detection of lithium, the test which has revealed its existence in a great variety of substances which had not been suspected of containing it, is the presence of one bright line, of a peculiar red, in the spectrum, seen on looking through a glass prism at a flame colored with a lithium compound.

490. Spectrum Analysis. — We have had occasion to observe that certain chemical substances, like boracic acid and salts of sodium, potassium, and lithium, impart peculiar colors to the blowpipe flame, or to any other hot and colorless flame. If these colored flames are looked at through a prism, a narrow pencil of the colored light being directed through a slit upon the prism, it will be seen that each different flame produces a peculiar spectrum, consisting of one or more distinct bright lines of colored light, and bearing no resemblance to the continuous band of rainbow colors which constitutes the common spectrum produced by a pencil from any source of white light. Thus, the spectrum of the yellow sodium flame consists of a single bright yellow line; that of the purple potassium flame contains two bright lines, — one lying at the extreme red, and the other at the extreme violet end, — and another, fainter red line; while the lithium spectrum consists of a very characteristic red line and a fainter orange line.

The peculiar lines which characterize the spectrum of any element are invariably produced by that element, and never by any other substance; and not only the color and number of lines, but their position in the normal spectrum, always remain unaltered. When the spectrum of a flame colored with a mixture of sodium and potassium salts is examined, the yellow line of sodium is seen in its place, and the red and purple lines of potassium are as visible in their respective positions as if no sodium had been present. This example illustrates one great advantage which the use of the prism gives. The unaided eye cannot distinguish the potassium color in the presence of the intense sodium yellow, the brighter color hiding the paler; but with the prism it is easy to detect each of several ingredients of a mixture by the appearance of its characteristic lines.

A special method of analysis, of extreme delicacy, is based upon these facts. Spectrum analysis is competent to detect the $\frac{1}{1000000}$ of a gram of sodium, or the $\frac{1}{1000000}$ of a gram of lithium, and many other elements in incredibly small proportions. So extreme is the delicacy of the method, that it brings into plain sight minute quantities which altogether escape the coarser processes of analysis, and reveals, as substances common in familiar things, elements which were long supposed to be of extreme rarity. Thus the presence of lithium, formerly considered a rare element peculiar to a few obscure minerals, has been demonstrated by spectrum analysis in many drinking waters, in tea, tobacco, milk, and blood. A still more striking illustration of the value of spectrum analysis is to be found in the discovery of a number of new elementary bodies by its means: among these elements are *rubidium*, *cesium*, *gallium*, *thallium*, *indium*, and others.

The methods and processes of spectrum analysis are not applicable to colored artificial lights alone: they have been applied, with encouraging success, to the lights of various quality which emanate from the sun, the stars, and the nebulae; but the details of these observations belong rather to physics than to chemistry.

491. Rubidium and Cesium (Rb and Cs).—These two elements are always found together, and in association with potassium. Though extensively diffused, they generally occur in very minute quantities. Rubidium seems to be rather the more abundant. Ten kilograms of the mineral water in which these metals were first discovered yield not quite two milligrams of cesium chloride, and about two milligrams and a half of rubidium chloride. The properties of both rubidium and cesium differ from those of sodium and potassium, not in kind, but only in degree. They are therefore classed with sodium and potassium as *alkali metals*. The atomic weight of rubidium is 85; and that of cesium, 132.

492. The Alkali Group.—The metals which must plainly be classed together under this head are sodium, potassium (ammonium), lithium, rubidium, and cesium. The common properties of the alkali metals are mainly these: they have the luster of silver, are soft, easily fusible, and volatile at high temperatures; they unite greedily with oxygen, and decompose water with facility, forming basic hydroxides which are very caustic and intensely alkaline bodies, not to be decomposed by heat; their carbonates, sulphates, sulphides, and chlorides, and indeed the vast majority of their salts, are soluble in water, and each metal forms but one chloride, one

bromide, and one iodide; they all form hydroxides, which act as bases, and never an acid hydroxide; they occur in nature in modes analogous, though not the same; their corresponding salts are often, though not always, isomorphous. There is a general, though not absolute, uniformity among the formulas of the compounds into which these elements enter; so that, if a compound of a given composition is proved to exist for one of these elements, the strong presumption is that analogous compounds with all the other elements of the group exist likewise with properties similar, though not identical.

The relations between the atomic weights of the alkali metals are interesting. That of sodium (23) is nearly the mean of those of lithium (7) and potassium (39); so also that of rubidium (85) is nearly half the sum of those of potassium (39) and cesium (132). In the case of the elements themselves and of their compounds, there is a gradation of properties coinciding with the gradation of their atomic weights.

THE CALCIUM GROUP.

CHAPTER XXV.

CALCIUM, STRONTIUM, AND BARIUM.

CALCIUM (Ca).—ATOMIC WEIGHT, 40.

493. The metal **calcium** is a constituent of several of the commonest and most important minerals: it forms a very considerable portion—perhaps as much as one sixteenth—of the solid crust of the earth. The metal itself is yellowish white, lustrous, and ductile, and suffers no change in dry air at the ordinary temperature. In moist air, it oxidizes quickly; and it decomposes water, with evolution of hydrogen. At a red heat, it melts, and, if oxygen be present, takes fire, and burns with a bright light. It is to be noted, that, unlike the metals of the alkali group, which are all univalent, calcium is a bivalent element.

494. **Calcium carbonate** (CaCO_3) occurs in nature in many different forms, sometimes finely crystallized, sometimes in an amorphous condition. Limestone, marble, calc-spar, and coral are calcium carbonate; the transparent crystalline Iceland spar is pure calcium carbonate. Chalk consists almost entirely of the shells of microscopic organisms; the shells of shellfish also are almost entirely composed of calcium carbonate; and this substance is an important constituent of dolomite, marl, and many other rocks and minerals. Ordinary *whiting* is chalk which has been purified by way of elutriation. Painter's putty is a mixture of whiting and a drying oil.

In all its varieties, calcium carbonate is readily attacked by acids, even if these be dilute. The action is attended with effervescence, owing to the expulsion of carbon dioxide and the escape of this gas through the liquid:—



495. Calcium carbonate, though tasteless, is slightly soluble in water, and the solution exhibits a faint alkaline reaction; it is, however, rather freely soluble in water charged with carbonic acid (§ 248).

Exp. 219.—Place in a test tube 20 or 30 drops of limewater, and as much pure water. In the mixture, immerse the delivery tube of a bottle from which carbonic acid gas is being evolved (Exp. 112, § 245). Calcium carbonate will be thrown down at first; but after a while, as the water in the test tube becomes saturated with the carbon dioxide, the precipitated carbonate will redissolve, and there will be obtained a perfectly clear solution, which, in spite of the large proportion of carbonic acid contained in it, has a decided alkaline reaction. By boiling the solution, so that a portion of the carbon dioxide may be expelled, the calcium carbonate can be again precipitated. So, too, if the liquid be left exposed to the air, it will gradually give off carbonic acid, and become turbid from deposition of calcium carbonate.

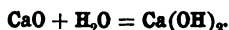
To the solubility of calcium carbonate in water containing carbonic acid, and to the fact that on the escape of the carbon dioxide the calcium carbonate is deposited, is due the formation of calcareous petrifactions, of stalactites and stalagmites, of the stones called *tufa* and *travertine*, and of many deposits of crystallized calcium carbonate. Whenever water charged with calcium carbonate flows out from the earth into the open air, or trickles into hollows or caverns within the earth, carbon dioxide is given off in the gaseous state, and calcium

carbonate is deposited. Stalactites are the pendant masses, like icicles, which hang from roofs of caverns, and arches, such as those under bridges and in cellars and other covered ways: stalagmites are the opposite masses, which grow up out of the drops of water which fall from the stalactites above them, before all the calcium carbonate has been deposited.

496. Calcium Oxide (CaO). — On being heated to a full red heat, calcium carbonate slowly gives off carbon dioxide, and is finally completely resolved into calcium oxide, commonly called *quicklime*, and carbon dioxide. For use in the arts, limestone is burned in special furnaces of peculiar construction, called limekilns, some of which are so arranged that they may be kept in operation for years without intermission.

Calcium oxide is infusible save at the intense heat of the electric arc, whereby it is melted and volatilized. It is therefore used for making crucibles in which the most refractory metals may be melted by the aid of the compound blowpipe.

497. Calcium Hydroxide (Ca(OH)₂). — When water is brought in contact with calcium oxide, the latter swells up and falls to powder; a large amount of heat is evolved; and there is obtained a compound of calcium, hydrogen, and oxygen, commonly called *slaked lime*, or, in chemical language, *calcium hydroxide*: —



Exp. 220. — Place a lump of recently burned quicklime, weighing about 30 g., upon a large earthen plate; pour upon the lime some 15 or 20 cc. of water, and observe how much the lime increases in bulk as it is converted into calcium hydroxide. The heat of the mass may be shown by thrusting an ordinary friction match into the middle of it: inflammation will ensue.

So much heat is developed during the union of water with lime, that wood will quickly be brought to the kindling temperature and inflamed, if it happen to be in contact with large masses of these substances reacting upon one another. Fires are very frequently occasioned by the access of water to ships or warehouses in which quicklime is stored. Under favoring conditions, finely divided, dry organic matter, such as sawdust, hay, rags, chips, or the dust on the floors of barns and factories, might be ignited by the slaking of very small quantities of lime, as could be shown by some slight variation of the above experiment.

498. Thermal Relations of Chemical Changes.—The development of heat as an incident to the chemical combination of water and lime is nothing more than a particular instance of a general law; viz., that, whenever and wherever chemical action occurs, energy in the form of heat is either set free or absorbed. It has been discovered, moreover, that the heat developed in any reaction is as definite in amount as are the weights of the reacting substances. It is a defect of chemical equations, as ordinarily written, that they tell nothing of the thermal changes which have occurred, but are confined merely to the expression of relations of weight.

Until recently the consideration of thermal changes, and the determination of the precise amounts of energy evolved as heat during chemical action, had been confined, in good part, to the students of a particular branch of science known as *thermochemistry*; but of late years much attention has been given to this subject, and the study of heat relations has become highly important in its bearings upon theoretical chemistry. Any considerable description of thermochemistry would be out of place in this book, but attention may still be called to a few general facts and definitions. Thus it seems to be a general principle of chemical action, that, when several reactions are possible, that one will take place which is accompanied with the greatest evolution of heat. In case, for example, hydrogen were made to act, under suitable conditions, upon a mixture of chlorine and bromine, there would be a reaction between the hydrogen and the chlorine, and hydrochloric acid would result; for, in the formation of this substance, more heat is evolved than is set free by the union of hydrogen and bromine. In other words, the heat of formation of hydrochloric acid (44,000 calories, § 22) is greater than that of hydrobromic acid (16,880 calories).

499. It has been found convenient to class reactions as *exothermic* or *endothermic*, according as heat is developed or absorbed when they occur. Any reaction in which heat is given out, as in the slaking of lime, is said to be exothermic, and the body resulting from such a reaction is an exothermic body. Attention has already been called to the development of heat, which is witnessed when hydrogen unites with other elements; and the unit of heat measurements was mentioned in connection with the combination of hydrogen and oxygen (§ 43), which is another example of an exothermic reaction, water being an exothermic body. Exothermic bodies are stable, and can only be resolved into their elementary constituents by the exhibition of an amount of heat or other form of energy equivalent to that set free when they are formed by the union of their elements.

Endothermic reactions are accompanied by absorption of heat, and the endothermic bodies are usually unstable. Sometimes they are highly explosive, as in the case of nitrogen iodide. In contrast with

ordinary oxygen, which is exothermic, ozone is an endothermic body. When ozone is formed by the polymerization of oxygen (§ 120), heat is absorbed, or, in other words, this form of energy (heat) is changed into the chemical force which serves to hold together the condensed molecules. But when the condensed molecules, which we call ozone, are split up into ordinary oxygen, the force which held them combined is set free in the form of heat: two molecules of ozone yield three molecules of oxygen, and 72,400 calories are evolved.

Some endothermic reactions are brought about by mechanical means, as by strong pressure, and others by the action of light.

500. When lumps of quicklime (calcium oxide) are exposed to the air, they slowly absorb both water and carbonic acid, and after a while fall to powder. This powder is known as *air-slaked lime*. When calcium hydroxide is stirred into water, there is formed not only a true solution (*limewater*) which may be obtained clear and colorless by filtration, but also a turbid liquor, consisting of particles of solid calcium hydroxide diffused through the limewater. This liquor is known as *milk*, or *cream*, of *lime*, according to its consistency. It is best prepared with hot water.

Both milk of lime and dry calcium hydroxide absorb readily carbon dioxide and hydrogen sulphide. For this purpose, they are used in the purification of coal gas. On this property of absorbing carbonic acid depends also, in great measure, the use of lime in mortar.

Mortar is commonly prepared by mixing 1 part of quicklime with water enough to form a thin paste, then adding 3 or 4 parts of coarse, sharp sand, and thoroughly incorporating these ingredients. The paste thus obtained is applied as a thin layer to the moistened surfaces of the bricks or stones to be united. The pasty mortar soon sets to the hard mass above described, and, on continued exposure to the air, it slowly absorbs carbonic acid at its surface, and is there converted into a compact compound of hydroxide and carbonate of calcium. The stonelike mass thus obtained binds firmly together the bricks or stones between which it has been interposed. The plastering used for finishing the walls and ceilings of rooms is mortar, to which a quantity of cow's hair has been added to increase its tenacity. In drying, plastering is, of course, subject to the same chemical changes as ordinary mortar. Newly built houses may be unwholesome for two reasons, even after the plastering seems to have dried out: first, because of dampness, due to the gradual giving-off of water

from the calcium hydroxide as fast as carbonic acid is absorbed; and also because the hair in the damp plastering slowly undergoes putrefactive decomposition for a time. It is noticeable that flies are often particularly abundant in newly plastered rooms.

501. Calcium hydroxide, like sodium or potassium hydroxide, exhibits a strong alkaline reaction when tested with moistened litmus paper, and exerts a corrosive action upon most organic substances: hence it is often called *caustic lime*. The value of lime as an ingredient of composts to be used as manure, depends on its neutralizing the acidity of the peat or other material, or, rather, on its making the mixture alkaline enough to be suitable for the growth and multiplication of the various microscopic organisms which cause the decay of organic matter.

Exp. 221. — Add a few drops of water to a small quantity of dry calcium hydrate, and rub it to a paste between the fingers. It will be felt that the alkali acts upon the skin: a little of the cuticle is really dissolved.

Lime is important from being not only the cheapest alkali, but the cheapest of all the bases. It is used in the manufacture of the caustic alkalies, soda and potash; of ammonia water and of bleaching powders; as a flux in many metallurgical operations; in the refining of sugar; for preparing a lime soap in the manufacture of stearine candles; and for numberless other purposes.

502. Calcium sulphate (CaSO_4) occurs in nature as the mineral anhydrite. The mineral gypsum is a hydrated calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The same hydrated salt may be obtained by adding sulphuric acid, or the solution of some sulphate, to a strong aqueous solution of almost any salt of calcium.

When gypsum is heated moderately, it is converted into the anhydrous calcium sulphate, which is often called *plaster of Paris*. If the anhydrous salt thus prepared be made into a paste with water, and then left to itself, it soon sets or hardens into a compact, coherent mass. This solidification is a consequence of the reassumption, by the calcium sulphate, of the two molecules of water of crystallization which were driven off by heat when the substance was made anhydrous.

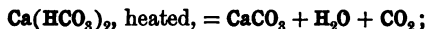
On account of this property, plaster of Paris is largely used for making casts of various objects. It is also used in the manufacture of stucco and of various imitations of marble.

503. Ordinary hydrated calcium sulphate is soluble in about 400 parts of water at the ordinary temperature. It occurs in sea water, and also in most well and spring waters. Water which contains any considerable amount of calcium salts, such as the carbonate and sulphate, or compounds of magnesium, is *hard*, and is not well adapted either for washing or for cooking.

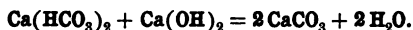
Exp. 222. — Dissolve a small bit of the hard soap of Exp. 149, § 317, in hot water, and add to the solution an equal bulk of a solution of calcium sulphate. The mixture immediately becomes turbid, and, after a few moments, there will be formed a greasy, flocculent, adhesive scum upon the surface of the liquor. This precipitate is *lime soap*.

Hard soap may be regarded as essentially sodium stearate. On the addition of calcium sulphate, the metals calcium and sodium change places, sodium sulphate and calcium stearate being formed. The latter, as has been seen, is insoluble in water. When soap is added to hard water, it will produce neither any permanent froth nor cleansing effect, until the sulphate, or other lime salt present, has all been decomposed. With such waters, much soap is consumed in removing the calcium compound, before the proper detergent action of the soap can be brought into play.

The hardness of water produced by the presence of calcium or magnesium carbonates is termed *temporary hardness*. Temporarily hard water may be softened by boiling; the excess of carbon dioxide, by virtue of which the salts are held in solution, being driven off, and the normal carbonates deposited, —



or, by the addition of “milk of lime,” which reacts with the acid carbonates, forming insoluble normal carbonates, —

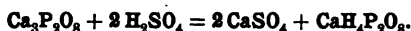


The presence of sulphates, and other soluble compounds of calcium and magnesium, causes what is termed *permanent hardness*. Such water cannot be softened by mere boiling, though, on heating the water strongly under pressure, in steam boilers, most of the sulphate can be thrown down.

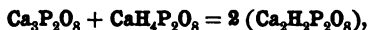
Hard water produces boiler crust and *scale* by the deposition of the salts present.

504. Calcium Phosphate.—The most important of the various calcium phosphates is the normal phosphate $\text{Ca}_3\text{P}_2\text{O}_8$, commonly called *bone phosphate*, because found in bones. It is the chief of the inorganic constituents of which the skeletons of animals are composed. Small portions of it are found in most rocks and soils (§ 182), it being a very widely diffused, though seldom a very abundant substance. Considerable masses of it have been found, however, in Spain, Canada, Florida, South Carolina, and many other localities, and it is the principal ingredient of some kinds of guano. As it occurs in bones, calcium phosphate is a valuable manure when reduced to a fine powder; for, though as good as insoluble in water, it dissolves readily in acids, and in solutions of various organic substances. But the mineral or rock phosphates, when ground to powder, are far less soluble than bone meal, and most of them need to be subjected to chemical treatment before they are applied as fertilizers.

When ground phosphate rock, spent boneblack, or bone ash, are treated with sulphuric acid, there is formed a quantity of calcium sulphate, and a soluble calcium acid phosphate ($\text{CaH}_4\text{P}_2\text{O}_8$), which is the artificial fertilizer known as *superphosphate of lime*,—



It is noteworthy, that, when carelessly prepared, and particularly when made from impure materials, a part of the soluble calcium phosphate may change, on keeping, to an insoluble form. In this case it is said to have *reverted*, or to have *gone back*. Thus, if quantities of bone phosphate and of superphosphate were mixed, and left in a heap, the following reaction would occur,



with formation of insoluble dicalcium phosphate. But the presence of this substance in a superphosphate is undesirable, because it acts in a different way from the soluble phosphate, and because it can be bought at a lower price than that at which the soluble phosphate is sold.

505. The reaction between sulphuric acid and bone phosphate, given above, is one step in the process of obtaining phosphorus. Burnt bones are treated with sulphuric acid, and the soluble calcium acid phosphate ($\text{CaH}_4\text{P}_2\text{O}_8$) is filtered from

the insoluble calcium sulphate, mixed with charcoal, dried, and ignited. The following reaction takes place: a portion of the phosphorus is set free and condensed under cold water, while the residue consists of a certain amount of calcium phosphate, identical in composition with that originally contained in the bone ash:—



506. **Calcium chloride** (CaCl_2) may be prepared by dissolving chalk or marble in hydrochloric acid (as in Exp. 101, § 245), and evaporating the solution to dryness. When dried at about 200° , calcium chloride is left as a porous mass, which is largely employed in the laboratory for drying gases (Appendix, § 16). When exposed to the air at the ordinary temperature, it soon absorbs so much water that it dissolves completely. At a low red heat, the anhydrous chloride melts to a clear liquid.

507. **Calcium fluoride**, or **fluor spar** (CaF_2), is used in the preparation of hydrofluoric acid, and sometimes as a flux in the reduction of ores. It occurs as a mineral, not infrequently in considerable quantities, especially in lead mines.

508. **Calcium hypochlorite** (CaCl_2O_2), as has been shown in § 101, is a component of the substance commonly called *chloride of lime*. This important bleaching agent is prepared by passing chlorine gas into chambers filled with layers of finely powdered slaked lime. Chloride of lime, or bleaching powder, is a dry, white powder, smelling feebly of hypochlorous acid. When exposed to the air, it slowly absorbs carbonic acid, and at the same time evolves chlorine; hence its employment as a disinfecting agent. If, instead of being left to be slowly acted upon by the carbonic acid of the air, it be treated with a dilute acid, such as vinegar, a copious evolution of chlorine will immediately occur. When heated, bleaching powder gives off oxygen, and calcium chloride is left as a residue.

Exp. 223. — Fill an ignition tube one third full of bleaching powder, and arrange the apparatus so that the gas may be collected over water. Heat the tube, and observe that the gas is expelled at a comparatively low temperature. 1 g. of bleaching powder yields 40 or 50 cc. of oxygen gas.

509. Calcium Sulphide. — There are several sulphides of calcium. The monosulphide, as prepared by heating a mixture of the sulphate and charcoal, or of the carbonate and sulphur, has the curious property of shining in the dark, after it has been exposed to light. The allied sulphide of barium behaves in a similar way. The substance popularly known as *luminous paint* contains one or another of these sulphides.

STRONTIUM (Sr), ATOMIC WEIGHT, 87; AND BARIUM (Ba), ATOMIC WEIGHT, 136.4.

510. The metals **strontium** and **barium** resemble calcium in appearance and properties. They are all bivalent elements. The specific gravity of calcium is 1.6, that of strontium 2.6, and that of barium 4; while the atomic weights are respectively 40, 87, and 136.4.

Most of the compounds of strontium and barium are closely analogous to the corresponding compounds of calcium. The oxides, peroxides, hydroxides, carbonates, sulphates, nitrates, phosphates, chlorides, sulphides, etc., resemble, in the main, the corresponding calcium salts. The hydroxides of strontium and barium are, however, more readily soluble in water than calcium hydroxide is, while their sulphates, nitrates, and chlorides are less soluble than those of calcium. Barium sulphate is almost absolutely insoluble in water, and strontium sulphate is only very slightly soluble. Barium sulphate is found native, sometimes in considerable masses, as a very heavy white mineral called *barytes*, or *heavy spar*, which, when powdered, is largely employed for adulterating white lead. The name *barium* comes from a Greek word meaning "heavy." Strontium salts are commonly prepared from the native carbonate, a mineral called *strontianite*; while the various salts of barium are obtained either from the native carbonate *witherite*, or more commonly from the sulphate.

The colors imparted to gas flames by the compounds of calcium, strontium, and barium, may be illustrated as follows:—

Exp. 224. — By means of iron wire, suspend three small bullets of well-burned coke from a ring of the iron stand. Heat the fragments in turn with the flame of the gas lamp, and observe the slightly yellowish flame which will be produced in each case; then moisten one of the pieces of coke with a solution of calcium chloride, the second with a solution of barium chloride, and the third with a solution of strontium nitrate, and again heat them in turn with the gas flame. The calcium salt will impart a reddish yellow color to the flame;

the barium salt, a green color; and the strontium salt, a beautiful crimson.

Nitrate and chloride of strontium are used for the preparation of red fires.

511. The members of the calcium group resemble each other closely in chemical and physical properties, though showing a marked gradation of properties in accordance with the gradation in atomic weights. In general, strontium and its compounds have properties nearly midway between those of calcium and of barium. The three elements form, in general, corresponding oxides, dioxides, and salts. Like the alkali metals, they decompose water at ordinary temperatures. The carbonates are decomposed by heat, calcium carbonate more readily than strontium carbonate, with the formation of the corresponding oxides. The nitrates and chlorides are all readily soluble in water, the calcium compounds more readily than the strontium, and the strontium than the barium.

THE MAGNESIUM GROUP.

CHAPTER XXVI.

MAGNESIUM, ZINC, CADMIUM, AND GLUCINUM.

MAGNESIUM (Mg).—ATOMIC WEIGHT, 24.

512. The compounds of **magnesium** are found widely diffused in nature, and are rather abundant. The bitter taste of sea water and of some mineral waters is due to the presence of magnesium salts; while magnesium silicate and carbonate are contained in a variety of minerals, and in such common rocks as dolomite, serpentine, soapstone, and talc.

513. **Metallic magnesium** may be prepared by heating magnesium chloride with metallic sodium in a crucible of porcelain or platinum, and subsequently dissolving out in cold water the sodium chloride which results from the reaction. It is also obtained in large quantities by the electrolysis of the chloride heated to fusion in crucibles. Magnesium is a lustrous metal.

as white as tin. It does not tarnish in dry air, though in damp air it soon becomes covered with a film of magnesium hydroxide. Cold water acts on magnesium only slowly; hot water acts more rapidly, magnesium oxide being formed, while hydrogen is set free. The metal dissolves readily in almost any acid, with evolution of hydrogen. It melts at a low red heat, and volatilizes at higher temperatures. It may readily be distilled at a bright red heat. When heated strongly in the air, it takes fire, and burns with a bluish white light of great brilliancy, and rich in chemically active rays. The metal is employed by photographers for illuminating caverns and other places into which sunlight cannot penetrate. The metal can be pressed into wire or into thin ribbons: a considerable quantity of it is now used in both these forms for purposes of illumination. In the form of a fine powder, it is used in the manufacture of the flash lights of the photographer.

514. Magnesium Oxide, or Magnesite (MgO).—There is but one compound of magnesium and oxygen: it is obtained as a white, amorphous powder when magnesium is burnt in the air, or it may be prepared by igniting the carbonate, chloride, or nitrate.

Exp. 225.—Roll 10 or 12 cm. of magnesium wire or thin ribbon into a coil around a small pencil; withdraw the pencil, and place in its stead a piece of iron wire or a knitting needle. Holding this wire horizontally, apply a lighted match to the end of the magnesium coil: the magnesium will burn to the white oxide, which coheres in an imperfect coil, clinging to the iron wire. A portion of the oxide goes off as white smoke.

The oxide is tasteless and odorless. It is altogether infusible at temperatures short of that of the oxyhydrogen flame. Very excellent crucibles, for scientific purposes, are prepared by compressing magnesium oxide into suitable forms; and the hard, compact oxide, obtained by calcining the native carbonate, is used as a lining for the converters in which steel is made.

515. Salts of Magnesium.—**Magnesium chloride ($MgCl_2$)** is found in sea water and many saline springs. Vast quantities of it are obtained as an incidental product at the potash works of Stassfurt. Much of it is used for *weighting* cotton goods, and hydrochloric acid may be cheaply prepared from it. On

heating magnesium chloride in tubes through which a current of steam is passing, decomposition takes place, and hydrochloric acid is set free, while magnesium oxychloride is formed. There is an inexhaustible bed of the double compound, known as *carnallite* ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$), at Stassfurt.

Magnesium sulphate (MgSO_4), or rather the hydrated compound ($\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$), is known as *Epsom salt*, on account of its occurrence in a mineral spring at Epsom, England. The sulphate occurs in other springs, and at Stassfurt in Germany. It is made artificially from various native minerals containing magnesium. It is a colorless, crystalline salt, readily soluble in water, and having a bitter taste. It is much used in medicine. If the crystallized magnesium sulphate ($\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$) be heated to about 120° , it loses six of its molecules of water of crystallization: the seventh is not expelled, however, until a temperature of 200° is reached. This last molecule of water is in some way differently related to the molecule from the others, and is known as *water of constitution*: it may be replaced by a molecule of an alkali sulphate, with the formation of double sulphates, such as $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$. The hydrate ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) occurs abundantly at Stassfurt as a mineral, called *kieserite*.

Magnesium carbonate (MgCO_3) occurs native as the mineral magnesite. The *magnesia alba* of the shops is a varying mixture of magnesium carbonate and hydrate, and is prepared by adding sodium carbonate to a hot solution of magnesium sulphate.

Magnesium sulphide is not formed in the wet way.

ZINC (Zn). — ATOMIC WEIGHT, 65.

516. Zinc does not occur in nature in the metallic state, but in combination with other elements, such as oxygen (*red oxide of zinc*) and sulphur (*zinc sulphide*, or *blende*): the carbonate and the silicate of zinc are also native minerals.

Zinc is a bluish white metal of crystalline texture, brittle at the ordinary temperature, and also when heated above 200° , but at a temperature of about 130° or 140° it may easily be rolled out or hammered into sheets. The metal melts at 425° ,

and boils at a bright red heat: in presence of air, the red-hot metal takes fire, and burns with a brilliant bluish white light, and formation of a dense cloud of white oxide of zinc.

If a strip of thin sheet zinc be held in the flame of the gas lamp, it can readily be burned to oxide. The experiment succeeds best with zinc leaf, which instantly burns with a vivid flame, and formation of floating flocks of the white oxide. In oxygen gas, zinc burns with peculiar brilliancy.

Exp. 236. — Mix intimately in a mortar 20 g. of dry granulated zinc (or zinc dust, if it can be obtained) and 40 g. of crude saltpeter; heat to redness a small Hessian crucible in an anthracite fire; remove the crucible from the fire, and place it in such position that any fumes which may subsequently be evolved from it shall be drawn into the chimney. By means of a spoon or ladle, project into the red-hot crucible the mixture of zinc and saltpeter, taking care to stand away as far as possible from the crucible. The greater part of the metal will burn fiercely, at the expense of the oxygen in the saltpeter, though a portion of it will be volatilized by the intense heat of combustion, and converted into zinc oxide in the air. The residue in the crucible is a soluble compound known as potassium zincate.

Granulated zinc is much used in the laboratory for a variety of purposes, but particularly for preparing hydrogen (§ 37). It may be prepared by melting the zinc in a Hessian crucible, and heating the melted metal nearly to redness. The crucible is then removed from the fire by means of appropriate tongs (Appendix, § 23), and its contents poured in a thin stream, from a height of 6 or 8 feet, into a vessel of cold water. This process of *granulation*, or *feathering*, may be conveniently applied to any of the other easily fusible metals, such as bismuth, lead, or tin, when they are required in a finely divided condition.

In the manufacture of zinc, a quantity of the vaporized metal is condensed in a very fine state of division, corresponding to the flowers of sulphur. This zinc dust (which contains also some zinc oxide) is used to a considerable extent in indigo dyeing in the manner illustrated by Exp. 190, § 430. It is a very convenient form of the metal for many experimental purposes. A small quantity may readily be prepared by shaking melted zinc in a small, thick wooden box. Thus, if a drop or two of molten zinc be poured into a thick pill box, the tightly closed box may be wrapped in a towel, grasped firmly in the hand, and shaken vigorously.

517. The vapor density of zinc is about 32.5, one half its atomic weight, 65: hence the molecule of zinc, when in the condition of a gas, consists of only one atom. The metal is

not much acted upon, either by moist or dry air, at the ordinary temperature, as it soon tarnishes, and becomes covered with a thin film of a basic carbonate of zinc, which adheres closely to the metal, and protects it from further change. Owing to this durability, metallic zinc is much used in the form of sheets. Sheet iron and iron wire also are often covered with a protecting coating of zinc, and are then said (most improperly) to be *galvanized*. Zinc forms several valuable alloys: brass is an alloy of zinc and copper, and German silver is a brass whitened by the admixture of a small proportion of nickel. The specific gravity of zinc varies from 6.8 to 7.3.

518. Zinc is readily attacked and dissolved by acids, in most instances with evolution of hydrogen. It dissolves also in potassium or sodium hydroxide solution, on boiling, setting free hydrogen, and forming *zincates*. The chemical action of dilute acids upon zinc is a very common source of that peculiar mode of force called a *galvanic current*. There are few, if any, chemical reactions which cannot be made to produce electricity; and, in general, the more powerful the chemical action, the more powerful is the electrical action which results.

Exp. 237. — Solder a piece of stout copper wire to one end of a strip of sheet zinc, 4 cm. wide by 10 cm. long. The soldering will be readily effected by rubbing the zinc and the wire, in the vicinity of the proposed place of contact, with a strong solution of zinc chloride, before applying the melted solder. In the same way, solder a similar wire to a like strip of bright sheet copper. Place the strips of zinc and copper in a vessel filled with water, acidulated with one twelfth to one tenth its volume of sulphuric acid, in such a way that the two strips shall not touch each other either within or without the liquid. As long as the wires coming from the strips of metal do not touch each other, the copper remains quiescent, while the zinc is attacked, and bubbles of gas rise from its surface; but if the two copper wires are brought into close contact, by means of a binding screw or by the application of solder, the following phenomena occur: 1. Minute bub-

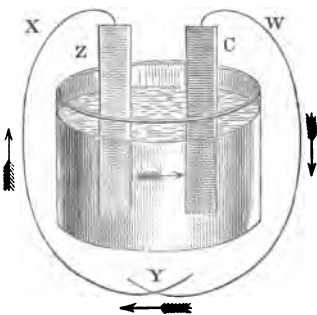


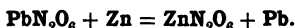
Fig. 82.

bles of hydrogen gas will be evolved from the surface of the copper plate; 2. The zinc dissolves more rapidly than before, and, at the close of the experiment, zinc sulphate may be recovered from the liquid in the beaker; 3. This transfer of the hydrogen from the zinc to the copper instantly ceases, if the contact between the wires is destroyed; 4. If the two wires be connected with the two ends of the coil of wire which surrounds the magnetic needle of the common galvanometer, the deflection of the suspended needle will demonstrate the fact that an electric current is passing through the wires from one plate of metal to the other.

This experiment well illustrates the principle on which a large class of batteries are constructed and worked, except that the corrosion of the zinc is generally hindered by coating it with mercury, or *amalgamating* it, as it is termed.

Beside the chemical method, there are several other ways of obtaining currents of electricity; notably, by transforming that form of energy which we call heat into the other form of energy known as electricity. For information upon this subject, the student is referred to books treating of that department of science known as *physics*.

519. When zinc is immersed in the solution of a lead salt, such as the nitrate or acetate, zinc dissolves, and lead is deposited in the metallic state, —



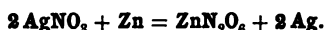
Exp. 228. — Dissolve 10 g. of lead acetate in 250 cc. of water; add a few drops of acetic acid in order to dissolve the cloudy precipitate of lead carbonate, which is formed from the carbonic acid in the water; pour the solution into a wide-mouthed bottle, and suspend in it a strip of sheet zinc. The zinc will soon be covered with a brilliant coating of crystalline spangles of metallic lead; and this *crystalline vegetation*, which is known as the *lead tree*, will continue to grow until all the lead has been deposited from the solution. The latter will now contain nothing but zinc acetate.



Fig. 83.

If, in this experiment, the piece of zinc be weighed before and after its immersion in the lead acetate, and if the precipitated lead be also weighed, it will be found that the weight of the lead obtained is to the weight of the zinc dissolved very nearly as 205.4 is to 65; that is, as the atomic weights of lead and zinc respectively. This experiment is interesting, as illustrating the general law of the replacement of one metal by another, according to a fixed proportion. When the

valence (§ 85) of the two metals is the same, this proportion is the ratio of the atomic weights; when the valence is different, the proportion is some multiple of this ratio. Thus, in the foregoing experiment, for every atom of lead precipitated, an atom of zinc was dissolved. In the analogous case represented by the following equation, one atom of zinc takes the place of two atoms of silver, —



520. **Electro-chemical Relations of the Elements.** — Many other substances beside the zinc and copper of Exp. 227, § 518, if brought into contact in a liquid capable of affecting them unequally, exhibit similar electrical phenomena. It is necessary that the substances should both be conductors of electricity, and that the liquid should contain some compound capable of such decomposition that there shall be formed a new compound containing one of the substances immersed in the liquid. When the two substances, as in Exp. 227, are connected by means of a copper wire, a current of electricity passes along the wire in each direction. The current which passes from the zinc to the copper in the liquid, and from the copper to the zinc in the air, is called the *positive current*, and under such conditions the zinc is said to be *positive* with reference to the copper.

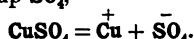
When the wire which connects the two plates is cut, the flow of electricity ceases; but, if the two extremities of the wires be immersed in some conducting liquid, the flow is reestablished. In many cases the passage of the current through a liquid effects its decomposition. The two extremities of the wires are called *poles*: that connected with the negative plate is called the *positive pole*, and that connected with the positive plate is called the *negative pole*. If the poles of a galvanic battery be immersed in a solution of zinc chloride (ZnCl_2), for example, this salt is decomposed by the action of the electrical current. The atoms of zinc go to the negative pole, and hence are called *positive* with reference to the atoms of chlorine, which are called *negative*, because they go to the positive pole. With reference to some other metals, as to magnesium, for instance, zinc is negative. The terms *positive* and *negative* are thus seen to be merely relative; and, under certain circumstances, the relation of one element to another may be directly reversed.

521. **Electrolysis.** — This decomposition of a chemical compound by an electric current is termed *electrolysis*. It is largely employed nowadays for obtaining several of the metals from their compounds, and in the various processes of electroplating.

Whenever a salt of a metal, in a fused or dissolved condition, is subjected to the action of an electric current sufficiently powerful to overcome the chemical force by virtue of which the atoms of the

molecule are held together, the compound is decomposed, as in the case of zinc chloride above mentioned, so that the metal separates, going with the positive current to the negative pole, while the acid radical, or nonmetallic element, in the case of binary compounds, separates at the positive pole.

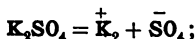
The salts of oxygen acids behave in a manner analogous to the halides; for example, when an electric current is passed through a solution of copper sulphate, the salt is decomposed into metallic copper and the oxidized group SO_4 , —



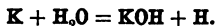
The oxidized group, in this case, cannot exist in a free state, and, owing to its instability, another reaction occurs: the group breaks up, oxygen is liberated, and the acid radical SO_3 reacts with the water of the solution to form sulphuric acid, —



the final result of the electrolysis being the deposition of copper at the negative pole, and the setting-free of oxygen and formation of free sulphuric acid at the positive pole. All neutral salts undergo a similar decomposition: the metal appearing at the negative pole; and the acid radical, or the results of its decomposition, at the positive pole. If the metal is capable of acting upon water, another reaction will, of course, occur; for example, if potassium sulphate be decomposed, the first action is, as in the case of the copper sulphate, the setting-free of potassium, and of the oxidized group or negative radical SO_4 , —



but, as stated above, SO_4 at once decomposes, and oxygen is set free as a gas at the positive pole, and free sulphuric acid also is formed. The separated metal in turn acts upon water, potassium hydroxide being formed, and hydrogen liberated at the negative pole, —



Many other compounds are decomposed in the same way as the metallic salts; for example, if a powerful electric current is passed through molten potassium hydroxide, it is decomposed, potassium appearing at the negative electrode, while water and oxygen, resulting from the hydrogen peroxide, which is formed at first, appear at the positive pole. Acids are similarly decomposed; in fact, in so far as this reaction is concerned, they may be regarded as salts of hydrogen.

There is evidently a close connection between the chemical and the electrical relations of the elements; but just what the relation is, is as yet unknown.

522. It is possible to arrange the chemical elements according to their electro-chemical characters, as ordinarily exhibited, so that each element in the series will be positive to any element placed above it, and negative to any one given below it. On this page the commoner elements are so arranged.

Speaking somewhat loosely, all the elements which in this list precede gold are negative, while gold and the elements which follow it are positive. We have been in the habit of speaking of the negative elements collectively, as the nonmetallic elements. The terms *negative* and *positive* are on some accounts to be preferred, although themselves not perfectly exact in their signification. The same element, in different compounds, will often play a very different part. Thus the element zinc, which we are now studying, acts in its compounds ordinarily as a positive element: its hydroxide (Zn(OH)_2) is a base; its oxide (ZnO) is a basic anhydride; and the element, when in combination, is usually combined with negative elements, or radicals, as, for example, in ZnCl_2 , ZnSO_4 , etc. Occasionally, however, zinc plays the part of a negative element; as, for instance, in potassium zincate (Exp. 226, § 516). In this compound, the zinc plays the same part that sulphur does in the sulphates, nitrogen in the nitrates, etc. Corresponding to potassium zincate (K_2ZnO_2), we should have zincic acid (H_2ZnO_2), and zincic anhydride (ZnO). In fact, the hydroxide of zinc does dissolve, either in acids (acting, therefore, as a base), or in alkalis (acting as an acid). Many of the elements which we generally designate as positive, or metallic, act in a similar manner. This difference of action is often accompanied by difference in *valence*. Thus in the case of chromium, as we shall see, we have two very distinct classes of compounds: (1) the salts of chromium, in which the atom of chromium (Cr) acts as a trivalent *positive* radical; (2) the chromates of various elements, in which the single atom of chromium (Cr) is hexivalent and negative. Corresponding to the former of these two classes, we have the basic oxide Cr_2O_3 , and the basic hydroxide Cr(OH)_3 ; corresponding to the second class, we have the acid anhydride CrO_3 , and the acid H_2CrO_4 .

523. The property which one metal possesses, of replacing another in its salts, as illustrated by Exp. 228, § 519, is an exhibition of their

Negative end — .

OXYGEN.
SULPHUR.
NITROGEN.
FLUORINE.
CHLORINE.
BROMINE.
IODINE.
PHOSPHORUS.
ARSENIC.
BORON.
CARBON.
ANTIMONY.
SILICON.
HYDROGEN.

GOLD.
PLATINUM.
SILVER.
MERCURY.
COPPER.
TIN.
LEAD.
COBALT.
NICKEL.
IRON.
ZINC.
MANGANESE.
ALUMINIUM.
MAGNESIUM.
CALCIUM.
SODIUM.
POTASSIUM.
Positive end + .

electrical relations. Metallic copper may be thrown down from a solution of one of its salts by the introduction of metallic iron or zinc. A little metallic mercury put into a solution of silver nitrate will cause the formation of a *silver tree*. In these cases the metal which goes into solution is said to be *electro-positive* to the metal which is precipitated, and the latter is *electro-negative* to the former.

524. **Equivalent Weights.** — In reactions like that of Exp. 228, § 519, where one metal replaces another, it is found that the replacement always occurs in fixed and definite proportions. In this particular experiment, the amount of lead deposited was to the amount of zinc dissolved as 102.7 to 32.5. If a solution of a salt of silver had been employed instead of the lead acetate, the amount of silver deposited would have been to the zinc dissolved as 107.1 to 32.5. The weights of the metals thus deposited or dissolved — that is to say, the amounts indicated by the numbers 102.7 and 32.5, in the case of lead and zinc — may be said to be the *equivalents* of each other: these numbers (or others bearing the same relation to each other) may be called the *equivalent weights* of lead and zinc respectively. The number of elements whose equivalent weights can be thus determined by the actual replacement of one by the other is limited; but, even in cases where two elements do not replace each other, their equivalent weights may still be determined by comparing each of the two elements with a third. In this way, by direct or by indirect means, we may draw up a table of the equivalent weights of the different elements. These equivalent weights would be either the same as the atomic weights, or some simple multiple or submultiple of them; for, by the very conception of the atomic theory, no replacement could take place except by a certain number of whole atoms.

525. Formerly, when there were no adequate data for determining, in certain cases, which multiple of the equivalent weight is the true atomic weight, chemists were forced to rest satisfied with the equivalent weights; hence, in some of the older works on chemistry, the student will find assigned to several of the chemical elements other weights than those given in § 633. Thus it was customary at one time to assign the weight 16 to sulphur instead of 32, 8 to oxygen instead of 16, etc. These weights are the equivalent weights just described, and they are still sometimes used by persons devoted to the practical applications of chemistry. For most purposes of calculation, it is immaterial whether the equivalent or the atomic weights be employed. Thus water is made up of 1 part by weight of hydrogen, for 8 parts by weight of oxygen; and it was formerly the custom to represent the equivalent weight of oxygen (8) by the symbol O. On this system, the symbol HO stood for water, and indicated that water contains hydrogen and oxygen in the proportion of 1 to 8, and that its equivalent weight is 9. But since

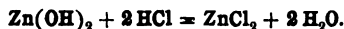
the molecule of water is held to contain two atoms of hydrogen and one atom of oxygen, the atom of oxygen weighing 16, the symbol of the compound is written H_2O . The proportion of hydrogen to oxygen is in both cases the same; and, in general, the relative proportion in which any two or more elements exist in a chemical compound, is a fact determined by analysis: it is a fact which no theoretical conceptions of ours can change. The atomic weights, however, or the values to be assigned to the symbols of the elements, are fixed by what we hold to be true with regard to the number of atoms in the molecule of the compound. Thus the formula of stannic chloride was formerly written SnCl_2 , in accordance with the old equivalent weight (59) of tin; but, now that we know that the atomic weight of tin is 118, the formula of stannic chloride must be written SnCl_4 , in order to express the same relative proportions of tin and chlorine.

In passing from the formulas of the older system to the corresponding formulas of the new, if the atomic weight of any element is double the old equivalent weight, it becomes necessary, in writing the symbol of any molecule containing this element, either to take half as many atoms of the element in question, or to take twice as many atoms of the other elements in the molecule, unless they also have had their combining weights doubled. It is a better knowledge of the molecular constitution of bodies than was accessible to their predecessors, that has led the chemists of the present day to employ, in the case of a considerable number of the elements, atomic weights which are multiples of the equivalents formerly in use.

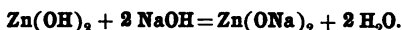
526. Compounds of Zinc. — Zinc oxide (ZnO) is formed when metallic zinc is burned in the air, and may also be prepared by igniting the carbonate. Under the name of *zinc white*, it is somewhat largely employed as a white paint. It dissolves readily in acids. When heated, it assumes a yellow color, but becomes white again on cooling.

Zinc hydroxide ($\text{Zn}(\text{OH})_2$) is precipitated from solutions of salts of zinc by alkaline hydroxides, and is soluble in an excess of the reagent. It is capable of acting both as an acid and as a base (§§ 67, 69); that is to say, it reacts with acids to form salts of zinc, and with strong bases, such as sodium and potassium hydroxide, to form zincates.

Exp. 239. — To a solution of zinc sulphate add carefully sodium hydroxide solution; filter, and treat a portion of the zinc hydroxide obtained with dilute hydrochloric acid. It dissolves readily, forming zinc chloride, —



Treat a second portion of the precipitated hydroxide with an excess of sodium hydroxide solution; warm the mixture, and, if necessary, boil it. If a sufficient quantity of the alkaline hydroxide be used, complete solution will take place, a sodium zincate being formed.



Zinc chloride (ZnCl_2) is a white, soluble, deliquescent substance, formed by dissolving zinc in hydrochloric acid. It is used for preserving timber, also in soldering, to cleanse the surface of the metal. *Basic chlorides*, or *oxychlorides of zinc* ($x\text{ZnO} \cdot \text{ZnCl}_2$), are approved cements. Dentists sometimes use them for filling teeth. Analogous magnesium basic chlorides also act as cements. **Zinc sulphate** (ZnSO_4), or rather the hydrated compound ($\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$) known as *white vitriol*, is used to a certain extent in medicine, and also in the arts. It is isomorphous with the similar compounds of magnesium and glucinum, and affords, like magnesium sulphate, a series of double salts with the sulphates of the alkali metals containing six molecules of water of crystallization. Zinc sulphide occurs in nature as zinc blende, usually colored by iron oxide or other impurities. Prepared in the wet way, it appears as a white, gelatinous precipitate, insoluble in water, acetic acid, and alkaline solutions, but soluble in hydrochloric and other mineral acids.

CADMIUM (Cd.) — ATOMIC WEIGHT, 111.4.

527. **Cadmium** is a comparatively rare metal, found associated with zinc in nature. It is remarkably similar to zinc in its chemical relations. It is a bluish white, lustrous metal, tarnishing somewhat when exposed to the air. It melts at 315° , and volatilizes at temperatures below redness. Heated in the air, it takes fire, and burns to a brown oxide (CdO). The vapor density of cadmium has been found to be rather more than 56. It is evidently half the molecular weight (111.4). As with zinc, the atom and the molecule of cadmium, in the gaseous condition, are identical. *Cadmium iodide* (CdI_2) is used in photography. *Cadmium sulphate*, like the sulphates of zinc and magnesium, forms double salts with the sulphates of the alkali metals, such as $\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6 \text{H}_2\text{O}$. *Cadmium sulphide* (CdS) is of a bright yellow color, insoluble in dilute acids and

alkaline sulphides. It has been used as a pigment, known as *cadmium yellow*.

GLUCINUM (Gl).—ATOMIC WEIGHT, 9.

528. **Glucium** is a rare metal, found, together with aluminum, in the emerald and in beryl, and a few other minerals. It may be reduced from its chloride by means of sodium. It forms an oxide (GlO), and yields a series of soluble, colorless salts, having a sweetish taste; hence its name. The sulphate (GlSO_4) crystallizes with seven molecules of water of crystallization, and is isomorphous with magnesium sulphate.

529. The metals of the magnesium group decompose water only at a high temperature. All of them are volatile at high temperatures, and they burn when heated in the air; all are capable of forming double sulphates with the alkali metals, which are isomorphous; and each of them forms only one series of salts, and but one oxide in which the metallic atom is bivalent. The salts of these metals resemble each other closely in respect to solubility, etc.; there being a gradation of properties, in accordance with the gradation in the atomic weights, similar to that noticed in the case of the members of the calcium group.

THE LEAD GROUP.

CHAPTER XXVII.

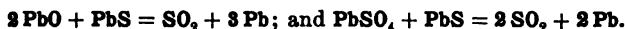
LEAD AND THALLIUM.

LEAD (Pb).—ATOMIC WEIGHT, 205.4.

530. The chief source of lead is the native lead sulphide (PbS), the ore called *galena*, which is tolerably abundant in many localities, and is often associated with barium sulphate, fluor spar, quartz, and other common minerals. It almost always contains a small proportion of silver sulphide. The carbonate of lead is also important as an ore in the United States.

From the sulphide it is possible to obtain metallic lead by a simple process of roasting and fusing. On heating galena moderately in the

air, a part of its sulphur burns off as sulphur dioxide, and there is left a mixture of oxide, sulphate, and sulphide of lead. If air be now shut off, and the heat of the furnace raised, the materials will react as in the following equations, and metallic lead will be left:—



Lead is a remarkably soft metal, of bluish white color. As is well known, it can readily be cut with a knife, and even be indented with the finger nail. It soils paper upon which it is rubbed. Its specific gravity is 11.4. It may be drawn into wire, and beaten into sheets, though, as contrasted with most of the other metals, it has but little tenacity. It melts at about 325° , and may be obtained in crystals by slowly cooling the molten metal.

The ready crystallization of lead once furnished a simple method of separating this metal from the silver, with which crude lead is almost always contaminated as it comes from the smelting furnaces. When melted argentiferous lead is allowed to cool slowly, and is at the same time briskly stirred, a quantity of solid crystalline grains separate out after a while, and sink beneath the liquid metal, whence they may be dipped out in colanders. These crystals are composed of lead nearly free from silver, while all but a trace of the silver contained in the original lead is left in that portion of the metal which has not yet solidified: in a word, the alloy of lead and silver melts at a lower temperature than pure lead. The lead crystals on the one hand, and the silver alloy on the other, were methodically remelted and recrystallized, until practically all the silver was concentrated in a rich alloy, from which the more precious metal was obtained by heating in a stream of air until all the lead was oxidized (process of cupellation), § 559.

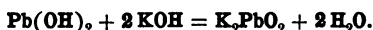
531. When in thick masses, such as the common sheets and pipes of commerce, lead is scarcely at all acted upon by cold sulphuric acid, and is not much corroded by cold hydrochloric acid. Both these acids form, by their action on the lead, difficultly soluble salts; and, as soon as a layer of the salt has once been deposited upon the surface of the metal, the latter is thereby protected from further corrosion. It is readily dissolved by dilute nitric acid, lead nitrate being formed. On exposure to the air, lead soon tarnishes, owing to the formation of a thin coating of a lead suboxide (Pb_2O). By the simultaneous or alternate action of water and air, lead is very

rapidly corroded, in consequence of the formation of a lead hydroxide, which is converted, by the carbonic acid of the air, into a carbonate. All natural waters act more or less on lead. In some cases the action is so slight, that lead pipes are used with safety for conveying the water; in other cases the use of lead pipes is very dangerous, on account of the poisonous character of the salts of lead.

532. Lead monoxide (PbO), commonly called **litharge**, may be obtained as a lemon-yellow powder by gently igniting the nitrate or carbonate. In the arts, litharge is prepared upon the large scale by heating metallic lead in a current of air. The color and texture of the product vary considerably, according to the temperature and other conditions under which the litharge has been prepared.

Exp. 230.—Heat a small fragment of lead upon charcoal in the oxidizing flame of the blowpipe, and observe the gray film of suboxide which forms at first, and the yellow incrustation of litharge which is obtained subsequently. The litharge may be melted, if a strong, hot flame be thrown upon it.

The monoxide reacts with acids to form salts, which resemble in some respects those of barium and strontium. It dissolves slightly in water as hydroxide, having a slightly alkaline reaction. With the strongest bases it reacts to form salts, called *plumbites*, which are analogous to the zincates. Plumbites of sodium and potassium may be obtained also by dissolving lead hydroxide (Pb(OH)_2) in caustic soda, or caustic potash solution, —



533. Other oxides of lead.—The **dioxide**, or **peroxide (PbO_2)**, is a dark brown powder formed by oxidizing litharge. The dioxide does not form stable salts with acids. When heated, it loses half its oxygen, and thus acts as a powerful oxidizing agent. It dissolves in concentrated potassium hydroxide solution, forming a salt of the formula K_2PbO_3 (potassium plumbate), evidently related to an acid, PbO(OH)_2 , of which several salts, called *plumbates*, are known.

Lead sesquioxide (Pb_2O_3) is produced as a reddish yellow, insoluble powder when sodium hypochlorite (NaOCl) acts on salts of lead, or on a solution of lead hydroxide in caustic soda.

Red Oxide of Lead. — Red lead, or *minium*, is apparently a combination of PbO and PbO_2 , approximating the formula Pb_3O_4 . It is obtained by heating litharge to a moderate red heat in air. By treating red lead with nitric acid, the monoxide may be removed, and the dioxide obtained.

Exp. 231. — Boil a small quantity of red lead with an excess of dilute nitric acid in a test tube or an evaporating dish, and observe that the red color disappears. Litharge is dissolved by the acid, while dioxide of lead is left as a brown powder.

Red lead is used in glass making, for coloring wafers and sealing wax, for painting iron work, and in printing wall papers.

534. Lead sulphide (PbS) occurs native in the form of galena, and it is thrown down as a black or dark brown precipitate when hydrogen sulphide is passed into the solution of a lead salt. On account of the deep color as well as the insolubility of this precipitate, hydrogen sulphide is often made use of as a means of detecting lead. The test is, in fact, so delicate, that solutions containing only a hundred-thousandth of their weight of metallic lead will assume a brown color on being charged with hydrogen sulphide. When hydrogen sulphide is passed through a solution of lead chloride containing an excess of hydrochloric acid, a compound of lead, sulphur, and chlorine is formed, which has a red or orange-red color, according to the conditions.

535. Other Salts of Lead. — **Lead Chloride (PbCl_2)** separates as a white precipitate when hydrochloric acid is added to a solution of a lead salt. The oxychlorides of lead are very numerous. One, having the composition $3\text{PbO} \cdot \text{PbCl}_2$, is a brilliant yellow substance, once used as a pigment, called *Turner's yellow*. **Lead acetate**, a soluble, readily crystallizable salt, is much used in the arts. It has a sweet, astringent taste, whence the name *sugar of lead*. Like other lead salts, it is highly poisonous.

Lead carbonate (PbCO_3), or rather compounds of the carbonate and hydroxide in varying proportions, are used to an enormous extent as a white paint, under the general name of *white lead*. One variety of this pigment may be made by dissolving litharge in acetic acid, and converting the basic acetate thus formed to a

basic carbonate by exposing it to carbonic acid gas. The native lead carbonate is an important ore of the metal.

Lead chromate (PbCrO_4) is a yellow, insoluble salt, used as a pigment, known as *chrome yellow*.

Lead silicate is of interest from being an important ingredient of flint glass. A certain proportion of it renders glass lustrous and very beautiful. Such glass is, however, soft and easily fusible. It is, moreover, rather easily acted upon by alkalies, acids, and other chemical agents, and is hence not well suited for use in the laboratory.

THALLIUM (Tl).—ATOMIC WEIGHT, 202.7.

536. Thallium is a malleable, ductile metal, resembling lead in external characters. It is found in certain varieties of iron pyrites. The properties of thallium are intermediate between those of lead and those of sodium and potassium. Like the alkali metals, it replaces hydrogen atom for atom.

Thallium forms two classes of compounds, — *thallous* compounds, in which it is univalent; and *thallic* compounds, in which it is trivalent.

THE COPPER GROUP.

CHAPTER XXVIII.

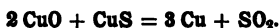
COPPER, MERCURY, AND SILVER.

COPPER (Cu).—ATOMIC WEIGHT, 63.

537. Though by no means one of the most abundant metals, **copper** is nevertheless very widely diffused in nature, and is largely employed by man. Traces of it exist in almost every soil, whence it is taken up by plants, in which it may almost always be detected by refined testing. Traces of it have repeatedly been found also in the various animal organs and secretions. Beside occurring in the native state, copper is found in a great variety of combinations. The most common of its ores, however, is the sulphide, or rather a compound of copper sulphide and iron sulphide in varying proportions,

known as *copper pyrites*. The carbonates and oxides of copper are also valuable as ores.

The process of obtaining copper from the oxygen ores or the carbonates is very simple, consisting in merely reducing the ore with carbon in a blast furnace. The ores containing sulphur are more difficult to reduce. In this case, the ore is repeatedly roasted to remove sulphur, and convert as much as possible of the sulphide into oxide. A mixture of the roasted ore and a proper flux is then melted down, yielding what is called a *matte* containing sulphides of copper and iron, and a slag containing the earthy impurities of the ore. The smelting is effected either in a reverberatory or a blast furnace. The matte resulting from this first smelting is roasted in a reverberatory furnace, and then melted, and the slag skimmed off. The furnace is allowed to cool somewhat, and the molten mass is subjected to the oxidizing action of hot air, to remove sulphur. The mass, now called *black copper*, a more or less pure cuprous sulphide, is again roasted, and fused in contact with air. During the first stage of the process, a portion of the sulphur is burned off, cupric oxide being formed, which, in the latter part of the process, acts upon the remaining sulphide, and metallic copper results, —



The crude copper thus obtained is refined by a peculiar process called *poling*.

538. Copper is a rather hard metal, of a well-known red color. It is very tenacious, ductile, and malleable. At the ordinary temperature, the metal is not altered in dry or moist air, unless finely divided. When heated in the air, it becomes covered with a coating of a black oxide. Metallic copper is not very readily acted upon by acids, excepting those rich in oxygen. Except when finely divided, it is scarcely acted upon by even concentrated hydrochloric acid. In hot sulphuric acid it dissolves as copper sulphate, sulphurous anhydride being given off; in nitric acid somewhat diluted, it dissolves readily as copper nitrate, and nitric oxide escapes (Exp. 27, § 53).

539. Several of the compounds of copper with other metals are of great importance in the arts. Brass, and the yellow metal used for sheathing wooden ships, are alloys of zinc and copper; bronze, gun metal, and bell metal are alloys of tin and copper, and various *compositions* are produced by mixing these alloys with brass. Copper is also an essential ingredient of all

the common coins, implements, and ornaments of gold and silver.

540. Cuprous and Cupric Compounds.—Copper forms two series of compounds, known respectively as *cuprous* and *cupric*. In the cupric compounds, the atom of copper is bivalent, as CuO , CuCl_2 , CuSO_4 . The cupric compounds, which comprise all the ordinary copper salts, are more stable than the cuprous bodies. The cuprous compounds are exceedingly unstable, and tend constantly to pass into the cupric condition. In the cuprous compounds, the element appears to be univalent, as, for example, in CuCl , CuI , Cu_2O , Cu_2S , etc.

It is possible that these formulas should be doubled, and written Cu_2Cl_2 , Cu_2I_2 , etc.; at present, however, we are justified in using the simpler formulas to express the cuprous compounds. Cuprous salts of the oxygen acids are unknown.

541. Oxides of Copper.—There are two oxides of copper. *Cuprous oxide*, *copper suboxide*, or *red oxide of copper* (Cu_2O), occurs in nature as *ruby copper*. It may be prepared artificially in various ways; as, for example, by the action of certain reducing agents on alkaline solutions of cupric salts (Exp. 171, § 384). Cuprous oxide is used to give a ruby-red color to glass. *Cupric oxide*, *copper oxide*, or *black oxide of copper* (CuO), may be prepared by heating the metal in a current of air, or by igniting the carbonate, hydroxide, or nitrate.

Exp. 232.—Bind a bright copper coin with wire in such manner that a strip of wire 8 or 10 cm. long shall be left projecting from the coin; thrust the free end of the wire into a long cork or bit of wood, and by means of this handle hold the coin obliquely in a small flame of the gas lamp. A beautiful play of iridescent colors will appear upon the surface of the copper, particularly if it be moved to and fro. Thrust the hot coin into water, and observe that it is at this stage covered with a red coating of copper suboxide. Replace the coin in the lamp, and hold it in the hot oxidizing portion of the flame: it will soon become black from the formation of cupric oxide. After a rather thick coating of oxide has been formed, again quench the coin in water: the black coating or scale of oxide will fall off, and beneath it will be seen a thin film of the suboxide firmly adhering to the metal.

Exp. 233.—Evaporate to dryness, in a porcelain dish upon a sand bath, some of a solution of copper nitrate prepared from copper, as in

Exp. 27, § 53. Place a small quantity of the dry residue upon a fragment of porcelain, and ignite it until red nitrous fumes are no longer given off. Cupric oxide will be left upon the porcelain.

542. Copper hydroxide ($\text{Cu}(\text{OH})_2$) is formed when caustic alkali is added to a solution of a salt of copper.

Exp. 234. — Place in a test tube or small bottle 8 or 10 cc. of a cold dilute solution of copper sulphate, and add to it enough of a solution of caustic soda to render the mixture alkaline to test paper. A light blue precipitate will fall. Cupric hydroxide is insoluble in water and in sodium hydroxide solution.

Exp. 235. — Repeat Exp. 234, with the difference that the solutions of caustic soda and copper sulphate are both heated to boiling, and are mixed while hot. Instead of the blue hydroxide, black cupric oxide will now be thrown down; for copper hydroxide readily parts with its water when heated, even if it be all the while immersed in water. It does not again combine with water after it has become cold.

Exp. 236. — Again repeat Exp. 234, but, instead of sodium hydroxide, add ammonia water drop by drop to the copper salt, and shake the tube after each addition of the ammonia. Cupric hydroxide will be precipitated, as before, in accordance with the reaction —



for, as has been said, this hydroxide is insoluble in water. But, since copper hydroxide is readily soluble in ammonia water, the precipitate will redissolve as soon as more of this agent than is needed to decompose the copper salt is added. The ammoniacal solution containing copper has a magnificent azure-blue color.

543. Copper sulphate (CuSO_4) may be obtained by treating metallic copper with hot sulphuric acid (§ 146), or by dissolving cupric oxide in dilute sulphuric acid. The salt crystallizes with five molecules of water. This hydrated salt is known as *blue vitriol* or *blue stone*, and is much used in the arts. A mixture of it with lime and water, known as *Bordeaux mixture*, has recently been found to be valuable as a fungicide. When thrown as spray upon vines and trees, this mixture destroys many hurtful fungi, and so promotes the formation of fruit. By applying it to growing potatoes, the crop may be protected from the ravages of the microscopic fungus which causes the disease called *potato rot*.

It is remarkable that the blue color of copper sulphate depends upon the presence of water.

Exp. 237. — Heat a little powdered blue copper sulphate upon a piece of porcelain. As it loses its water, the light blue powder will turn white. A drop of water upon the anhydrous powder will restore the blue color.

544. When ammonium hydroxide is added to a solution of copper sulphate in sufficient excess to dissolve the hydroxide at first formed, the liquid changes to a deep blue color (Exp. 236, § 542). This solution contains a body having the composition expressed by the formula $\text{CuSO}_4 \cdot 4 \text{NH}_3 \cdot \text{H}_2\text{O}$. On heating this salt, it loses water and ammonia, and a body having the composition represented by $\text{CuSO}_4 \cdot 2 \text{NH}_3$, known as *cuprammonium sulphate*, results, which may be regarded as ammonium sulphate, in which two hydrogen atoms are replaced by one (bivalent) atom of copper. Many similar compounds are produced when soluble copper salts are treated with ammonium hydroxide.

545. Copper Chlorides. — There is a *cupric chloride* (CuCl_2) and a *cuprous chloride* (CuCl).

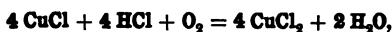
Cupric chloride is prepared by treating cupric oxide or carbonate with hydrochloric acid: it crystallizes from its solution with two molecules of water, in brilliant green needlelike crystals, and is very soluble in water. When strongly heated, it gives off half its chlorine, and is changed to cuprous chloride.

Cuprous chloride is most conveniently obtained by passing sulphur dioxide through a mixed solution of copper sulphate and sodium chloride, when it separates as a white powder. Cuprous chloride is insoluble in water, but readily soluble in ammonia water, forming a colorless liquid, which becomes blue on exposure to the air, owing to the absorption of oxygen. The ammoniacal solution of cuprous chloride possesses the remarkable property, also, of absorbing carbon monoxide, and is used in the analysis of gases for this purpose.

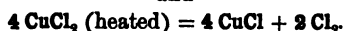
Cuprous chloride is sometimes used as a reducing agent. An oxychloride of copper of variable composition, known as *Brunswick green*, was once used as a pigment.

546. An interesting method of obtaining chlorine on the manufacturing scale, as proposed in England several years ago, was based on the fact, that, under certain conditions, the two chlorides of copper may readily be changed one into the other. Thus, when hydrogen chloride (HCl) and air are brought into contact with dry copper

chlorides at such a temperature (near 400°) that the tendency of cuprous chloride to absorb chlorine, and that of cupric chloride to evolve chlorine, are equally balanced, both these reactions will occur as follows:—



and



The chlorine may be used for the manufacture of bleaching powder (§ 508). No very large quantity of the copper compound is needed, but there must be an extended surface of it. To this end, pieces of brick were saturated with copper sulphate, which speedily changed to the chloride when put to use. The chamber filled with these fragments was kept at the proper temperature.

547. Copper acetates are formed by the action of acetic acid upon metallic copper exposed to the air. They are commonly called *verdigris*. Verdigris is usually prepared by packing plates of copper between woollen cloths steeped in vinegar. The term is often, although incorrectly, applied to the green coating of a basic carbonate which forms on metallic copper when long exposed to moist air. **Copper arsenite** ($\text{Cu}_3(\text{AsO}_3)_2$) is a green powder, known as *Scheele's green*. It is obtained by the addition of sodium arsenite to a copper solution. A compound of arsenite and acetate of copper is known as *Schweinfurt green*, or *Paris green*. Admixed with diluents, it is much used in this country as an insecticide. **Copper sulphides** (Cu_2S and CuS) occur native; and the double sulphide of copper and iron, called *copper pyrites*, has already been mentioned as an ore of copper. **Cupric sulphide** (CuS) is of considerable importance to the analyst: it is formed when hydrogen sulphide is passed into a solution of a cupric salt, and is a black powder, insoluble in water, in dilute acids, and in alkaline solutions. When moist, it oxidizes in the air to the sulphate.

548. All soluble compounds of copper are active poisons, and great care should be taken to keep copper or brass vessels which are used for cooking perfectly bright and clean; as oily matters, and even weak vegetable acids, while they have no action on the clean, bright metal, dissolve the oxide and carbonate quite readily. An antidote for poisoning by copper salts is the white of egg.

MERCURY (Hg).—ATOMIC WEIGHT, 198.5.

549. Small globules of metallic **mercury** are sometimes found in nature; but the principal ore of this metal is the sulphide (**HgS**) called *cinnabar*, which is found in large deposits in Idria and at Almaden in Spain, and at New Almaden in California. From this sulphide the metal is readily extracted by roasting the ore, and condensing the vapor in vessels of iron or in brick chambers; or the ore may be distilled with lime and iron turnings in cast-iron retorts. The sulphur is retained by the lime or iron, as the case may be; while metallic mercury passes off in the state of vapor into receivers containing water, beneath which it condenses to the liquid state. The crude mercury is redistilled to purify it. Large quantities of mercury are used in extracting gold and silver from their ores, for silvering mirrors, and in the process of fire gilding. Preparations of mercury are employed also as medicaments, and for various purposes in the useful arts. The fluidity of the metal makes it valuable in the construction of certain philosophical instruments, of which the thermometer and barometer are familiar examples.

550. At the ordinary temperature of the air, mercury is a brilliant, mobile liquid, of 13.6 specific gravity. It freezes at -39.4° , becoming a ductile solid of tin-white color and granular fracture, which can be cut with a knife. Mercury vaporizes slowly, even at ordinary temperatures, and boils at about 360° . The specific gravity of mercury vapor has been found to be somewhat less than 100, while its atomic weight is 198.5. The symbol **Hg** thus denotes the two-volume weight of this element (§ 170), and the molecule of mercury is regarded as containing but a single atom.

551. Pure mercury is unacted upon by the air at the ordinary temperature. When heated, it is converted into the red oxide. It is not attacked by hydrochloric acid; hot sulphuric acid converts it into mercuric sulphate; it dissolves readily in nitric acid.

552. **Compounds of Mercury.**—There are two **oxides** of mercury,—an unstable, black **mercurous oxide** (**Hg₂O**), and the

ordinary red mercuric oxide (HgO). This latter oxide, as commonly prepared by heating mercury in the air, or by gently heating mercuric nitrate, is a compact, granular, almost crystalline, glistening powder, of bright brick-red color; but when prepared in the wet way, by adding caustic alkali to a solution of a mercuric salt, it is, when dry, a soft, orange-colored powder. Mercuric oxide is decomposed by heat, as has already been seen (Exp. 3, § 9). Corresponding to the oxides of mercury are two series of compounds,—the *mercuric* salts, in which the atom Hg is bivalent; and the *mercurous* salts, in which the atom Hg is univalent. These compounds are analogous to those in the similar series of copper compounds; but, unlike copper, mercury forms two series of salts derived from oxygen acids. Thus there is a *mercurous nitrate* (HgNO_3), and a *mercuric nitrate* ($\text{Hg}(\text{NO}_3)_2$), while, as regards copper salts of oxygen acids, only cupric compounds are known.

553. **Mercuric sulphide** (HgS), which occurs native as cinnabar, is the most important ore of mercury. An artificial product of the same composition, known as *vermilion*, is used as a pigment. The sulphide is readily obtained by passing hydrogen sulphide into a solution of a mercuric salt. Thus prepared, it is of a black color. It is insoluble in water, in dilute acids, and nearly insoluble in alkaline liquids.

554. **Mercurous chloride** (HgCl), commonly called *calomel*, is extensively used as a medicament. It is a heavy, white powder, which volatilizes at temperatures below redness without previous fusion. It is tasteless, odorless, and, like cuprous chloride and silver chloride, is as good as insoluble in water. It turns black when wet with ammonia water.

555. **Mercuric chloride** (HgCl_2), better known by the name of *corrosive sublimate*, commonly occurs in commerce in translucent, crystalline masses. It melts at about 265° , forming a colorless liquid, which boils at 293° . The fumes are acrid, and, like the salt itself, exceedingly poisonous. When ammonia is added to a solution of mercuric chloride, the body called *white precipitate* is thrown down. The composition of this substance may be represented by the formula NH_2HgCl .

Mercuric chloride unites with many organic substances to

form compounds insoluble in water and imputrescible. It coagulates albumin, for example, and the more perishable portions of wood; hence the employment of raw white of egg as an antidote in cases of poisoning by corrosive sublimate, and the use of the mercury salt for preserving wood, — a purpose for which it would, no doubt, be largely employed were it not for its high cost. Collections of dried plants, and of other objects of natural history, are preserved both from the attacks of fungi, which might cause the decay thereof, and from the attacks of insects, by brushing over the specimens an alcoholic solution of the chloride. It is a valued antiseptic agent, and is used by surgeons in very dilute solutions (1 to 1,000) to cleanse instruments, etc., in order to prevent contamination of wounds in surgical operations.

Mercuric iodide (HgI_2) is formed by the direct union of mercury and iodine, or when potassium iodide is added to a solution of a mercuric salt, as a bright red powder. It is readily soluble in a solution both of potassium iodide and of mercuric chloride, so that an excess of either of the reagents must be avoided in obtaining it. Upon warming the red iodide to 150° , it sublimes in yellow prismatic crystals, which change to red again, slowly if left untouched, or immediately if rubbed with any hard substance.

556. Amalgams. — Mercury unites with most of the other metals to form alloys, many of which are pasty, or even liquid, when the proportion of mercury contained in them is large. These alloys are commonly called *amalgams*, in contradistinction to the ordinary solid alloys of the other metals, in which mercury has no place. The liquid amalgams are true solutions of other metals, or of solid amalgams, in the fluid mercury. The so-called *silvering* of mirrors is an amalgam of tin. *Sodium amalgam* is largely used in extracting gold and silver from their ores. *Ammonium amalgam* is a remarkable substance, formed by treating sodium amalgam with a strong solution of ammonium chloride. The ammonium amalgam is a very voluminous, spongy mass, having a metallic appearance. It is exceedingly unstable, rapidly decomposing into mercury, ammonia, and hydrogen.

Mercury may be detected in almost any soluble salt of the element by introducing into a solution of the salt a piece of clean copper.

Exp. 238. — Place a drop of a solution of either of the nitrates or chlorides of mercury upon a copper coin, and rub the liquid over its surface. A white coating of metallic mercury will be deposited upon the metal.

All mercury compounds are decomposed when heated in a closed tube with dry sodium carbonate, the mercury condensing upon the sides of the tube in metallic drops; or, if a bit of clean copper wire be held in the upper part of the tube, it will become coated with a mercury mirror.

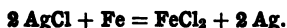
SILVER (Ag).—ATOMIC WEIGHT, 107.1.

557. Silver is a widely diffused and a somewhat abundant element. It frequently occurs native, both pure and alloyed with mercury, copper, and gold. The metal more commonly occurs in combination with sulphur, mixed with sulphides of lead, antimony, copper, and iron. It is from argentiferous sulphides that the larger part of the silver of commerce is extracted, and among ores of this kind the argentiferous lead sulphide (galena) is abundant. Combinations of silver with selenium, tellurium, chlorine, bromine, and iodine, are also to be enumerated among silver-containing minerals. Of these, the chloride (horn silver) occurs in quantities large enough to make it valuable as an ore of the metal. A small proportion of silver exists in sea water (about 1 mg. in 100 l.); and its presence has been recognized in common salt, in chemical products in the making of which salt is used, in various seaweeds, in the ashes of land plants, in the ash of ox blood, and probably also in coal. In sea water it exists, as sodium and potassium do, in the form of chloride.

558. Silver is much more familiarly known in the form of an alloy than in any other compound. Known from the earliest ages, the metal has always been prized as much for its beauty as for its utility. White, brilliantly lustrous, susceptible of an admirable polish, wonderfully malleable and ductile, the best-known conductor of heat and electricity, and permanent in the air whether hot or cold, wet or dry, it represents and

embodies in the completest sense all that is commonly understood by the term *metal*. Though fusible only at a high temperature, it may be readily volatilized in the electric arc furnace.

559. The method of obtaining silver from its ores depends upon the character of the ore. Sometimes the silver is amalgamated with mercury. Thus, in one of the so-called *amalgamation processes*, crushed sulphide ores are mixed with salt and roasted, whereby the silver is converted into chloride. The chloride thus formed is reduced to metallic silver by treating with scraps of iron and water,—



When the reduction is complete, mercury is added, which forms an amalgam with the silver, that can be drawn off from the earthy material, and the excess of mercury squeezed out. On heating the amalgam in iron retorts, the mercury distills over, and silver is left behind.

Many silver ores are smelted in furnaces, and an alloy of lead and silver obtained, from which, by one or another metallurgical process, there is prepared a concentrated product, rich in silver, but which still contains much lead. To set free the silver, this argentiferous lead is placed in shallow cups, or basins, lined with bone ash, wood ashes, or marl, and strongly heated in such manner that a free current of air shall play upon the surface of the molten metal. The lead is oxidized to litharge, which melts and continually flows away; while new quantities of the alloy are added from time to time, until finally a ball of pure, bright silver is left in the cup. This process is known as *cupellation*; and it is often employed for assaying silver in the laboratory, though in this case the *cupel* is made of pure bone ash, which absorbs the whole of the melted litharge.

In the case of some ores, several extremely complicated methods of extracting silver are employed.

560. Silver combines slowly with chlorine, bromine, and iodine, and promptly with sulphur. It is easily soluble in nitric acid, and dissolves slowly in hot sulphuric acid; but it is little acted upon by hydrochloric acid, owing to the comparative insolubility of the chloride. The tarnishing of silver is due to the formation of a thin film of the black sulphide over the metallic surface by combination between the silver and the sulphur of the hydrogen sulphide, which is often present in the air of towns and houses. In the case of salt spoons and saltcellars, silver is apt to be discolored by the action of

sodium chloride. Silver is almost as heavy as lead, its specific gravity being 10.5.

561. The physical and chemical qualities of silver fit it to serve as a medium of exchange, and as the material of jewelry and plate. Since the pure metal would be rather too soft for ordinary use, it is hardened by combining with it a small proportion of copper. The proportion of copper in the *standard* silver employed for coinage varies in different countries: in the United States, France, and Germany it is 10 per cent, while in Great Britain it is 7.5 per cent.

Exp. 239. — Put a small silver coin into a small flask, and cover it with nitric acid diluted with two parts of water. Warm the flask gently in a place where there is a good draught of air: the coin will gradually dissolve, with evolution of a gas (nitric oxide), which, on contact with air, produces the abundant red fumes which escape from the flask. Add more nitric acid from time to time, if necessary, to complete the solution. The blue solution contains both the silver and the copper dissolved in nitric acid.

Place in the blue solution one or two copper coins, and leave the flask at rest for some days in a warm place. Then collect the little plates of pure silver, which have separated from the solution, upon a filter, and wash them, first with water, and then with ammonia water, until the ammonia water no longer shows any tinge of blue. This silver, washed finally with water, and dried, is well-nigh pure. If it be again dissolved in nitric acid, the solution will contain nearly pure silver nitrate.

562. **Silver Nitrate (AgNO_3).** — This salt, as we have already seen, is obtained in solution by dissolving silver in nitric acid. When such a solution is evaporated to the point of crystallization, the nitrate is obtained in transparent, anhydrous, tabular crystals, which are soluble in their own weight of cold water, and in half their weight of hot water. The fused salt is used in surgery as a caustic, under the name of *lunar caustic*.

Silver nitrate, when pure, is not altered by exposure to sunlight; but, if it be in contact with organic matter, light readily decomposes it, and a black, insoluble product is formed of no ordinary stability. Hence the solution of the nitrate stains the skin black, and the salt forms the basis of an indelible ink used for marking linen and other fabrics. Silver nitrate is much used in photography.

563. Silver chloride (AgCl) occurs native, sometimes in cubical crystals, and sometimes in compact, semitransparent masses, which, from their general appearance, have given the mineral the name of *horn silver*. Silver chloride may be precipitated from any soluble silver salt by adding hydrochloric acid or the solution of any soluble chloride to the silver solution. Silver chloride is insoluble in water and acids, but is dissolved by ammonia water, potassium cyanide, sodium thiosulphate, and strong solutions of the alkaline chlorides. Exposed to the light, it is partly decomposed, and becomes dark colored.

Silver iodide and bromide are prepared by adding a solution of a soluble iodide or bromide to a solution of some silver salt.

Exp. 240. — Fill three test tubes one third full of water, and pour into each a few drops of a moderately strong solution of silver nitrate. Add to the first test tube 2 or 3 cc. of a solution of sodium chloride, and shake the tube violently: a dense, white, curdy precipitate of the silver chloride will be produced. Add to the second test tube 2 or 3 cc. of a solution of potassium bromide, and shake the tube: a yellowish precipitate of silver bromide will be thrown down. Add to the third test tube 1 or 2 cc. of a solution of potassium iodide, and shake up the liquid: a pale yellow flocculent deposit of silver iodide will be formed.

Withdraw from each test tube a portion of the precipitate it contains, and try to dissolve each precipitate in moderately strong nitric acid: the attempt will fail, for these silver salts are insoluble in nitric acid.

Withdraw from each test tube another portion of the precipitate it contains, and treat each precipitate with ammonia water: the silver chloride will dissolve easily, the bromide less easily, the iodide with difficulty. Lastly pour upon the remnants of the original precipitates in the three test tubes a moderately strong solution of sodium thiosulphate: all three precipitates will immediately dissolve.

Exp. 241. — Precipitate some curdy silver chloride by adding sodium chloride solution, or hydrochloric acid, to a solution of silver nitrate so long as any precipitate is produced. Throw the precipitate upon a filter, and wash it with water; then open the filter, spread the chloride evenly over it, and place it in direct sunlight. The white precipitate rapidly changes to violet on exposure to the sun's rays, the depth of shade increasing as the action of the light continues. Upon the facts illustrated in this and the preceding experiments, the main processes of photography depend.

The changes produced by this action of light upon silver compounds evidently depend upon acts of reduction, though they are not yet thoroughly well understood. The study of the subject is not a little complicated by the fact that silver is capable of existing in several allotropic forms, one or another of which may be obtained, according as different reducing agents are made to act upon silver salts. The properties of the allotropic forms of silver differ widely from those of the common or normal metal, which may, perhaps, be a polymerized form of the more active varieties of the metal.

564. Other Silver Compounds.—*Silver oxide* (Ag_2O) corresponds to cuprous oxide (Cu_2O). It is decomposed below a red heat, giving up its oxygen. The hydroxide (AgOH) is very slightly soluble in water, giving an alkaline reaction. At 60° it is converted into the oxide (Ag_2O). So-called *oxidized silver* is silver coated with a thin film of sulphide by dipping in a solution of potassium sulphide.

Silver cyanide (AgCN) is a white powder insoluble in water. It is soluble in potassium cyanide, forming a double cyanide of potassium and silver; and, so dissolved, it is used in electroplating. *Silver sulphide* (Ag_2S) occurs as a native mineral. *Silver sulphate* (Ag_2SO_4) is formed when metallic silver is boiled with strong sulphuric acid. The action which takes place is—



565. Photography.—The chemical changes which the salts of silver undergo when exposed to light are the basis of the art of photography, not because these are the only salts which are affected by light, but because none are so advantageous, on the whole.

There are two entirely distinct processes by which photographs on glass are obtained,—the *wet plate* and the *dry plate*. In the wet-plate process, a glass is coated with a thin film of collodion, containing a small amount of soluble iodides and bromides. This coating is made by pouring a solution of the collodion in alcohol and ether upon the clean dry plate, and allowing the solvents to evaporate. As soon as the film of collodion is coherent, the plate is dipped into a bath of silver nitrate, slightly acidified, and allowed to remain a few minutes, until a certain amount of silver iodide or bromide is formed in the film; the plate is then immediately exposed, in the camera, to the action of light for a short time. When removed, no image is visible; but, on pouring over the film a solution of a reducing agent, such as pyrogallic acid or ferrous sulphate, the image will appear. This

development of the image will take place more or less rapidly, according to the strength of the developing solution, the intensity of the light, and the length of exposure. The image produced on the plate will be what is known as a *negative*; that is, an image in which those parts which were most brilliant in the object photographed are darkest, and the darkest shadows show as unchanged iodide or bromide of silver. These unchanged silver salts must then be dissolved out of the film. This is done by means of a solution of "hyposulphite of soda": the plate will then show the image in opaque and transparent portions, with many gradations between. After thorough washing, to remove the hyposulphite, the plate is dried, and the negative is thus finished. This wet-plate process, requiring the use of a sensitizing bath, and a dark room at the spot where the plate is to be exposed, is very inconvenient for landscape work, and is now almost completely displaced by the dry-plate process.

In this process, the silver salts are disseminated through a film of gelatine; and the plates, if kept from the action of light, may be preserved in an active condition for a long time. The film is prepared by melting together a mixture of gelatine with a soluble bromide or iodide, or both, and then adding, with stirring, a certain proportion of silver nitrate, which will cause the precipitation of very finely divided iodide and bromide of silver throughout the mass of gelatine. The melted mass is then allowed to flow evenly over the surface of glass plates; and these films, when cool and hard, are ready for use. After exposure in the camera, the image must be developed in the same way as in wet plates, by the action of reducing agents, which may be a solution of ferrous oxalate, or of pyrogallie acid or hydroquinone, or many other agents; but the plates may be kept for some time after exposure, before development, without injury to the quality of the negative, if not exposed to light. After development, the unchanged silver salts must be dissolved out of the film with hyposulphite of soda, and the film then be thoroughly washed and dried, to obtain the negative. The gelatine film is sometimes put upon thin sheets of celluloid, so that it may be wound upon rolls, and used for taking many pictures before recharging the holders, by simply winding the film from one roll to another, and thus presenting a fresh sensitized surface before the lens of the camera. Orthochromatic or isochromatic plates are dry plates which have been treated with a weak solution of some dye, — a treatment which increases the sensitiveness of the silver salts to certain parts of the spectrum. In this way, contrasts of light and shade are often shown more accurately than could be accomplished by the use of an ordinary plate.

From the negative obtained by either of the processes described, positive pictures on paper may be printed in any number desired. For this purpose, the surface of the paper must be prepared with a

layer of silver chloride; and, in the ordinary photographic paper, this is done by first coating with a film of albumin, to prevent the silver salts from sinking too deeply into the substance of the paper. After drying, the paper is floated on a solution of sodium or ammonium chloride, and then, after drying again, it is floated on a solution of silver nitrate, to obtain a film of silver chloride. After drying, the paper is exposed under a negative to the action of light until the picture is clearly printed out. The print is then removed from under the negative, and, after washing, is transferred to the *toning bath*, which is usually a slightly alkaline bath containing gold chloride. In this bath, a portion of the silver reduced by the action of light is replaced by gold, and the reddish tone of the print is changed to a purplish black tint. After the toning is complete, the print is washed, and then soaked in a solution of hyposulphite of soda, to dissolve out the unchanged silver salt. Finally, a long-continued washing in water, which is constantly renewed, must be given, in order to remove the last traces of the hyposulphite of soda, as any trace of this salt is injurious to the keeping of the finished print. After drying, the print is ready for mounting.

Other processes for obtaining prints depend upon the sensitiveness of salts of iron and platinum to the action of light, and some papers are used which require development in the same manner as a negative after being exposed. These variations and the details of the various manipulations may be studied in special works relating to photography. Skill in the art can only be obtained by long practice.

566. The three elements, mercury, copper, and silver, do not decompose water under any circumstances. Each forms two oxides, basic in character, which, except in the case of copper, are readily decomposed by heat. Copper and mercury form two series of salts, in one of which the atom of the metal is bivalent, in the other univalent. Silver is seldom bivalent, but forms some compounds corresponding to the cupric bodies. All three elements are readily acted upon by nitric acid and by strong sulphuric acid, while they are but little affected by hydrochloric acid.

RARE METALS.—THE CERIUM GROUP.

567. Scandium (Sc), Yttrium (Y), Lanthanum (La), Erbium (Er), Cerium (Ce), Neo-didymium (Nd), Praseo-didymium (Prdi), Samarium (Sm), Terbium (Tb), Ytterbium (Yt), and Thulium (Tu) are a group of elements seldom found except in certain rare minerals, which occur principally in Scandinavia and the United States. They are mainly

of theoretical interest. The existence of scandium was predicted by Mendelejeff (§ 636) long before its discovery. In properties, the compounds of these elements are generally related more or less nearly to those of aluminum. Cerium oxalate is used as a medicament. A preparation of lanthanum deposited on a net of asbestos is used for increasing the efficiency and diminishing the heat of gas flames. The lanthanum compound acts to convert into light a part of the heat generated by the combustion of the gas. The two didymiums are interesting, in that the resemblances between them are analogous to those seen in the case of cobalt and nickel (§ 604). It is not improbable that some of the so-called elements of this group are complex mixtures of several elementary bodies that have not yet been isolated.

CHAPTER XXIX.

ALUMINUM, GALLIUM, INDIUM, MANGANESE, IRON, COBALT, NICKEL, CHROMIUM, TUNGSTEN, URANIUM, MOLYBDENUM.

ALUMINUM (Al).—ATOMIC WEIGHT, 27.

568. **Aluminum** is perhaps the most abundant element upon the earth's surface, next to oxygen and silicon. It is the most abundant of all the metals, as much as a twelfth of the solid crust of the globe being composed of it. It occurs in enormous quantities, in combination with oxygen and silicon, in most rocks and soils. It is contained in clay, marl, and slate, as well as in feldspar, mica, and many other common minerals.

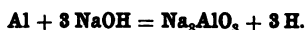
Although the compounds of aluminum are so abundant, it is only recently that methods of obtaining the metal cheaply have been devised. For this reason it has not yet been generally applied to many uses for which it is well suited. The preparation of aluminum from its ores—those principally employed being cryolite, sodium aluminum fluoride ($3 \text{ NaF} \cdot \text{AlF}_3$), corundum, aluminum oxide (Al_2O_3), and bauxite ($\text{Al}_2\text{O}_3 \cdot 2 \text{ H}_2\text{O}$)—was long considered to be a very difficult process. One method was to melt cryolite in suitable vessels, and introduce metallic sodium into the molten mineral, when the vapor of the sodium united with the fluorine, and aluminum was set free. Another method of procedure is to form a double chloride of aluminum and sodium ($3 \text{ NaCl} \cdot \text{AlCl}_3$) by heating cryolite with common salt, or by passing chlorine gas over a mixture of clay, charcoal, oil,

and salt, heated to bright redness, and reducing the chloride thus formed by means of metallic sodium in a properly constructed furnace. Several processes recently introduced depend upon the use of the electric current in special furnaces. One of these methods consists in passing a powerful electric current through a molten mixture of aluminum oxide and fluorides of sodium and aluminum, the aluminum oxide being dissolved in the fused flux. The furnace used is in the form of an open, iron-cased box, thickly lined with carbon, and so arranged that the melted aluminum can be run off at the bottom. A series of bars of carbon are arranged so as to dip into the furnace, forming the positive pole, while the furnace itself forms the negative pole. By the action of the electric current, the aluminum oxide is decomposed: the oxygen, combining with the carbon of the positive pole, passes off as carbon dioxide; while the metallic aluminum, being heavier than the molten mass, sinks to the bottom, and is drawn off from time to time. The process is a continuous one, new portions of the aluminum oxide being added as fast as the material is used up.

To obtain **aluminum bronze**, an alloy of aluminum and copper, a fire-clay box provided with large carbon terminals is filled with broken pieces of coke mixed with aluminum oxide and metallic copper, and an electric current is passed into this mixture. By the intense heat produced by the interruption of the current, the whole mass is raised to a very high temperature, and the aluminum reduced by the hot carbon forms an alloy with the copper. The same process may be employed to obtain other aluminum alloys.

569. Aluminum is a bluish white metal, of remarkable lightness. Its specific gravity, 2.56, is nearly the same as that of porcelain, and about a quarter of that of silver. The metal is malleable, ductile, and tenacious, and may be beaten into thin sheets, like gold and silver, and drawn into fine wire. It melts at a temperature lying between the melting points of zinc and silver, but is not volatile except in the electric arc. It conducts electricity much better than iron, and heat even better than silver. It is remarkably sonorous: a bar of it, suspended by a wire, rings with a clear musical note on being struck. In the air, aluminum undergoes very little alteration, even at a strong red heat. It may be melted in open crucibles without oxidation, and readily cast into any desired form. Unless it is in the form of a fine powder, the metal is not much acted on by nitric or sulphuric acids, though

it dissolves rapidly in hydrochloric acid. It is soluble also in strong solutions of sodium and potassium hydroxide, hydrogen being set free, and salts called *aluminates* formed, —

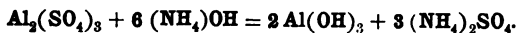


570. Aluminum is used for the barrels of opera glasses and telescopes, and many other purposes where lightness and strength are of importance. Aluminum bronze, an alloy of copper, is exceedingly hard, but is malleable and as tenacious as steel. It has a golden color, and is susceptible of being highly polished. Its firmness and elasticity render it suitable for the beams of balances and numerous other purposes.

571. **Aluminum oxide**, or **alumina** (Al_2O_3), occurs native as the minerals corundum, ruby, and sapphire. Emery is impure corundum, much used for grinding and polishing. Alumina is the only oxide of aluminum known.

572. **Aluminum hydroxide** ($\text{Al}(\text{OH})_3$) may be obtained as a gelatinous, flocculent precipitate by adding ammonia water to the solution of an aluminum salt. When heated moderately, the hydroxide loses some of its water, and is converted into AlO_2H , sometimes termed *meta-aluminic acid*, of which several salts are known. Some of these compounds occur as minerals, as, for example, calcium meta-aluminate ($\text{Al}_2\text{O}_4\text{Ca}$), magnesium meta-aluminate ($\text{Al}_2\text{O}_4\text{Mg}$), in the mineral spinel, zinc meta-aluminate, and others. The hydroxide ($\text{Al}(\text{OH})_3$) dissolves readily in acids, forming aluminum salts; it also dissolves in caustic alkalies, forming a class of salts called *aluminates*: that is to say, it acts as a base towards acids, and as an acid towards strong bases.

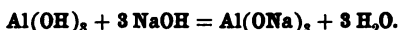
Exp. 242. — Heat a small fragment of aluminum sulphate (common alum will answer equally well) with water in a test tube until it has completely dissolved; pour half the solution into another tube, and add to it, drop by drop, ammonia water, until the odor of ammonia persists after the mixture has been thoroughly shaken. Aluminum hydroxide will be precipitated in accordance with the reaction —



Put two or three drops of the moist aluminum hydroxide into another test tube, and cover them with ammonia water: no clear solu-

tion will be obtained, for aluminum hydroxide is but slightly soluble in ammonia water.

Put two or three drops of the moist aluminum hydroxide into still another test tube, and cover them with a solution of sodium hydroxide: the precipitate will dissolve immediately; sodium aluminate is formed, and this salt is easily soluble:—



Exp. 243.—Take another portion of the clear solution of aluminum sulphate prepared in Exp. 242, and add to it, drop by drop, a dilute solution of caustic soda. A precipitate will soon fall, as in Exp. 242, and, if no excess of sodium hydroxide were added, this precipitate would persist; but, on adding more of the soda solution, the precipitate dissolves at once, with formation of sodium aluminate (Al(ONa)_3).

Sodium aluminate is largely used by calico printers as a mordant (§ 574). It is often obtained nowadays by fusing aluminum oxide with sodium carbonate. As thus prepared, it has the composition AlO_2Na .

573. Aluminum hydroxide combines readily with many organic coloring matters, forming substances insoluble in water.

Exp. 244.—Take a small quantity of the solution of cochineal prepared in Exp. 193, § 432, add to it an equal bulk of a solution of aluminum sulphate (or of common alum), and then add to the mixture ammonia water, as in Exp. 242, § 572. A colored precipitate, consisting of aluminum hydroxide and of the coloring matter of the cochineal, will be thrown down: it is the substance called *carmine lake*. Similar precipitates may be prepared by substituting almost any other organic coloring matter for the cochineal of this experiment. Precipitates thus formed, by the union of a metallic hydroxide and a coloring matter, are classed as *lakes*.

574. Mordants.—The fiber of cotton, when impregnated with alumina, or with basic salts of aluminum, can be made to retain colors which the cotton itself has no power to hold (Exp. 195, § 435); hence the use of aluminum salts as *mordants* in dyeing. In fact, mere immersion in a solution of a salt of aluminum suffices to make a great difference in the amount of coloring matter taken up by cotton. An acetate of aluminum is much employed in dyeing, because, when exposed to the air on the cloth, it is partly decomposed: a certain amount of acetic acid is set free and volatilized, leaving the fibers impregnated with aluminum hydroxide or oxide.

Exp. 245. — Prepare some aluminum acetate as follows: Dissolve 6 g. of sugar of lead (lead acetate) in 8 cc. of hot water; also dissolve 8 g. of common alum in 12 cc. of hot water. Mix the two solutions, and filter off the insoluble lead sulphate which is formed. In the solution thus prepared, soak a piece of cotton cloth, and then hang it up in a moist and warm atmosphere for several days. Treat this cloth, as well as a piece of ordinary cotton of the same size, with a solution of logwood, as described in Exps. 195, 196, § 435, and observe the difference in the amount of color imparted to the fabric.

Other oxides, or hydroxides and basic salts, beside those of aluminum, are used as mordants. An iron acetate, made by dissolving scraps of iron in the crude pyroligneous acid obtained by the destructive distillation of wood (§ 369), is much used by dyers. Salts of tin, of chromium, and of other elements, are employed to a greater or less extent.

575. Aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3$) is prepared by treating hot roasted clay or shale, which are aluminum silicates, with sulphuric acid. The mixture of aluminum sulphate and silica obtained is called *alum cake*; and from it the aluminum sulphate can be obtained by treating with water, which dissolves the aluminum sulphate, and leaves the silica behind. Aluminum sulphate is employed as the source of the various compounds of aluminum used in dyeing and calico printing. A number of basic aluminum sulphates are known.

576. Alums. — *Potassium alum* is an aluminum potassium sulphate, crystallizing in sharply defined crystals. Its composition is represented by the formula $\text{AlK}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$. It is known as *common alum*, although of late years *ammonium alum* has to a considerable extent taken its place. The formula of ammonium alum is $\text{Al}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$. Large quantities of these alums are used in dyeing, calico printing, and paper making. They are often prepared by treating roasted clay, or schist, with sulphuric acid, and adding potassium sulphate or ammonium sulphate to the solution, which is then left to crystallize. Much alum is made also by roasting certain aluminous schists charged with iron pyrites (FeS_2) and carbonaceous matter. Heaps of the schist are fired, and allowed to burn slowly, so that a part of their sulphur may unite with the oxygen of the air, and go to form aluminum and ferric sulphates. To the concentrated solution of these sulphates a strong solution of potassium chloride is added, whereupon alum is deposited, while the extremely soluble, noncrystallizable ferric chloride remains in the mother liquor.

There are many other alums, one of which will be described on

another page. Some twenty-five different alums have been prepared; and nearly one hundred are possible, not counting those obtainable from compound ammonias. They are all soluble in water, and crystallize therefrom in the form of octahedra. The general formula for the class is $M''M'(RO_3)_2 \cdot 12H_2O$, in which M' may stand for Li, Na, K, Rb, Cs, Ag, or NH_4 , and the like; while M'' may stand for Al, Ga, In, Cr, Fe, Mn, or Co, and R may stand for either S or Se. All the alums are isomorphous (§ 488), and capable of crystallizing together, either admixed or layer by layer. By transferring a crystal of one kind of alum to a strong solution of another kind, it is easy to cover the first crystal with a layer of the second alum; and the process might be repeated with a third and a fourth, or with any number of alums. In this way a colorless alum may be coated with a colored alum, or a small crystal of a colored alum may be made to serve as a nucleus, and left at the center of a large crystal of a colorless alum.

577. **Aluminum chloride** ($AlCl_3$) may be made by heating alumina with charcoal in chlorine, or by passing vapor of carbon tetrachloride over red-hot alumina. Aluminum chloride is volatile at high temperatures, and distills over, together with gaseous carbon oxides. It combines with alkali chlorides to form double halides (§ 118), from which, as has been seen, metallic aluminum can be prepared.

578. **Aluminum Silicates.**—Of all the aluminum compounds, the silicates are by far the most important. Clay, in all its varieties, is a hydrated aluminum silicate, usually mixed with an excess of silica, beside other impurities derived from the rocks from whose decomposition the clay itself has been formed. Clay is remarkable, on account of its plasticity when moist, of the facility with which it is converted into stonelike masses when strongly heated, and of its infusibility when pure.

Earthenware, bricks, and ordinary pottery are made from common clay by mixing the clay with water enough to form a plastic paste, which is then molded into any desired form, dried, and intensely ignited. The red color of certain varieties of ware is due to the iron oxide they contain. Porcelain is made from a very pure clay (kaolin). The glaze on articles of pottery is made by coating them with an easily fusible substance, such as a mixture of litharge and clay, or, in the case of porcelain, finely ground feldspar, and subjecting them, thus coated, to high heat. Ordinary stoneware is glazed by throwing common salt into the kiln. The salt volatilizes, and, coming in con-

tact with the heated ware, it is decomposed, and a fusible silicate results, which renders the articles impervious to moisture.

The blue pigment **ultramarine** was formerly obtained from the mineral lapis lazuli, a mixed silicate of aluminum containing sulphur. An artificial ultramarine is nowadays manufactured in large quantities by heating together sodium sulphate, feldspar, sulphur, and some rosin or similar substance. By the use of less sulphur, a green ultramarine may be obtained.

Hydraulic cement may be prepared by igniting a mixture of limestone, clay, and powdered quartz. The powdered product, when stirred up with water, soon hardens. The setting or hardening of such cements depends upon the formation of silicate and aluminate of calcium. Much of the cement employed for ordinary purposes is obtained by burning certain varieties of impure limestone, which, as experience has shown, contain clay, lime, and silica in the right proportions.

GALLIUM (Ga), ATOMIC WEIGHT 69.5; and INDIUM (In), ATOMIC WEIGHT, 113.

579. **Gallium** is a rare element found as a sulphide in some zinc ores. The oxide (Ga_2O_3) and the hydroxide ($\text{Ga}(\text{OH})_3$) closely resemble the corresponding aluminum compounds, as do the various salts of gallium. The sulphate forms a double salt with ammonium sulphate, analogous to common alum.

580. **Indium** is a rare metal, found associated with zinc in certain ores. It is a soft, white metal. It forms an oxide (In_2O_3) and an hydroxide ($\text{In}(\text{OH})_3$) similar to those of aluminum in chemical properties, and in general the element resembles aluminum closely in its properties and those of its salts.

581. The three elements aluminum, gallium, and indium are sometimes known as the *aluminum group*. Their oxides of the composition R_2O_3 are all feebly basic, and their sulphates form double salts (alums) with the sulphates of the alkali metals. Each of these elements has a valence of three, as a general rule.

MANGANESE (Mn).—ATOMIC WEIGHT, 55.

582. **Manganese** is a grayish white, hard, brittle metal, which oxidizes very readily, and is slightly magnetic. Its principal ore is the dioxide (MnO_2), which has already been employed in the generation of oxygen (Exp. 4, § 12) and of chlorine (Exp. 44, § 93). The residue, in the latter case, consisted of manganese chloride, which may be obtained in pink crystals ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) by filtering the liquid left in the flask, and evaporating it until it is ready to crystallize.

Enormous quantities of manganese chloride are formed at chemical works when chlorine is prepared on the large scale, and it is often desirable to recover the dioxide from these waste liquors. This purpose might be accomplished by heating the liquor, under pressure, with chalk, and subsequently exposing the moist manganous hydroxide to hot air, in order that it may take up oxygen; but a better method is to neutralize the waste chloride with limestone, in order to precipitate impurities, such as iron hydroxide, and to mix the clear liquor with an excess of milk of lime. A muddy precipitate of manganous hydroxide ($\text{Mn}(\text{OH})_2$), admixed with the excess of lime employed, is thrown down, which, on being exposed to a blast of steam and air, becomes black, through oxidation of a part of the manganese compound. On pouring upon the blackened mass a quantity of manganous chloride, part of the excess of lime is removed in accordance with a reaction, which may be written, —



The calcium chloride is run off after the mixture has been allowed to settle, and the sediment is used for making chlorine by causing it to flow into stills charged with hydrochloric acid.

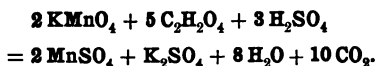
583. With oxygen, manganese forms several compounds, — *manganous oxide* (MnO), from which are derived the *manganous salts*, such as MnCl_2 , MnSO_4 , and the other common salts of manganese; *manganese dioxide* (MnO_2), to which are related some exceedingly unstable *manganic salts*, such as manganic chloride (MnCl_4), which change readily to the corresponding manganous compounds; *manganic oxide*, or manganese sesquioxide (Mn_2O_3), which forms a few unstable salts, the most interesting of which is manganese alum, isomorphous with common alum, but containing manganese in place of aluminum; *manganous-manganic oxide* (Mn_3O_4), which occurs in nature, and is formed when the other oxides are ignited in the air; *manganese trioxide* (MnO_3), an exceedingly unstable substance, decomposing at the ordinary temperature, which may be regarded as the anhydride of *manganic acid* (H_2MnO_4).

584. **Manganic acid** has never been obtained in a free state. Several of the *manganates*, however, are well-known bodies. Indeed, there are some reasons why even manganese dioxide (MnO_2) might be regarded as a manganic manganate: —



Potassium manganate (K_2MnO_4) may be made by fusing together manganese binoxide, caustic potash, and potassium chlorate. The manganate is soluble in water, the solution being of a green color. When this green solution is boiled, *potassium permanganate* (KMnO_4) is formed, which gives a dark purple colored solution. The manganates and permanganates readily give up oxygen, and lose their color; even a piece of wood or paper, thrown into the green or red solution of a manganate or permanganate, will quickly abstract oxygen from the solution, and destroy its color. Potassium permanganate is largely employed as a germicide, notably for disinfecting putrid water, as well as animal or vegetable matters in a condition of putrefaction. *Condy's fluid*, sold as a disinfectant, is a solution of potassium permanganate. The oxidizing action of potassium permanganate may be shown by the following experiment.

Exp. 246.—In a beaker or flask dissolve 0.25 g. of crystallized oxalic acid in 50 cc. of water, add 5 cc. strong sulphuric acid, and warm the solution to about 60° . Then add a solution of potassium permanganate *drop by drop*, and observe that the color is at first immediately destroyed. Continue to add the permanganate until it is no longer decolorized. The reaction that has taken place may be thus represented:—



The oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) is entirely converted into water and carbonic acid: the potassium permanganate gives up its oxygen, and is converted into a mixture of manganese and potassium sulphates.

On this property of potassium permanganate are based methods for the quantitative estimation of readily oxidizable substances, such as oxalic acid and iron, i.e., the ferrous salts.

Manganese heptoxide (Mn_2O_7) is the anhydride of permanganic acid (HMnO_4), which may be obtained as a dark green liquid by treating potassium permanganate with sulphuric acid.

It will be noticed that the higher oxides of manganese are acid anhydrides, while the lower oxides show basic properties. The variation in the valence of manganese, from two in the manganous compounds to seven in the permanganic compounds, is worthy of attention.

IRON (Fe). — ATOMIC WEIGHT, 55.6.

585. Although iron is one of the most widely diffused and most abundant of the metals, no great amount of it is found in the metallic state. Meteors, however, fall upon the earth from outer space, which consist mainly of metallic iron, contaminated with several other elements in small proportions. Minerals containing iron occur in great numbers; and there are, indeed, few natural substances in which iron is not present. It is found in the ashes of most plants, and in the blood of animals. The natural compounds of iron which are available as ores of the metal are chiefly oxides and carbonates.

From the richer iron ores a very excellent iron can be obtained by simply heating the broken ore with charcoal in an open forge fire, urged by a blast. The ore is deoxidized by the carbon of the fuel, and the reduced iron is agglomerated into a pasty lump, called a *bloom*; while the earthy impurities contained in the ore combine with a portion of the oxide of iron to form a fusible glass, or slag. This process is not economical in the chemical sense, for much iron is lost in the slag, and much fuel is burned to waste in an open fire; but, when well conducted, it yields an admirable quality of iron, and is easily practiced by people possessing but little mechanical skill and no chemical knowledge. It is undoubtedly the oldest method of extracting iron from its ores.

586. In the extraction of iron from its common ores, the metal is usually obtained, not pure, but in a carburetted fusible state, known as *cast iron* or *pig iron*. The main features of the process are, first, a previous *calcination* or *roasting*, to expel water, carbon dioxide, sulphur, and other volatile ingredients of the ore; secondly, the *reduction* of the oxide of iron to the metallic state by ignition with carbon; thirdly, the *separation* of the earthy impurities of the ore by fusion with other matters into a crude glass, or *slag*; and, lastly, the *carbonizing* and melting of the reduced iron. The preliminary calcination is not always essential; but with many ores, especially the carbonates and hydroxides, it is very desirable. Not infrequently all the drying necessary is effected in the upper part of the

blast furnace itself, within which the last three steps of the process always take place.

The blast furnace for iron consists essentially of a double cone, built of fire brick and masonry, and is from 25 to 90 feet in height, and from 15 to 18 feet in width at its broadest part. An idea of its construction may be obtained from Fig. 84. The furnace is closed at the bottom, the air necessary for the support of the combustion being supplied by a powerful blast blown through pipes called *tuyères* (pronounced *tweers*). At the high temperature produced, the carbon of the fuel removes the oxygen from the iron ore, and the metallic iron is set free. The reduction of the oxide of iron, however, is not alone sufficient to secure the metal. Iron ores almost always contain earthy admixtures, consisting chiefly of silica, clay, and calcium carbonate; and these substances are so intimately mixed with the reduced metal, that it is essential to melt them before the iron can separate by virtue of its greater specific gravity. This is brought about by converting these impurities into fusible double silicates by the addition of some proper substance, which is called a *flux*. With ores in which the earthy admixture is chiefly calcareous, the flux must be clay or some siliceous material; but in the more frequent case of ores containing clay or silica, the flux will be limestone or quicklime. In either case, a fusible double silicate of aluminum and calcium is the essential constituent of the slag.



Fig. 84.

The blast furnace is charged at the top with alternate layers of the fuel (which may be charcoal, anthracite, or coke), the ore, and the flux, which is generally lime; and air is constantly supplied in immense quantities at the bottom of the furnace. The blast coming in contact with a great excess of incandescent carbon, there is formed immediately carbon monoxide; and this gas, together with the unaltered nitrogen, ascends the shaft. The layers of solid material thrown in at the top of the furnace gradually sink down, and, as soon as a stratum of ore has descended sufficiently to be heated by the hot mixture of nitrogen and carbon monoxide, it becomes reduced to

spongy metallic iron, which, mixed with the flux and the earthy impurities of the ore, settles down to hotter parts of the furnace, where it enters into a fusible combination with carbon, while the flux and earthy impurities melt together to a liquid slag. The liquid carburetted iron settles to the very bottom of the furnace, whence it is drawn out, at intervals, through a *tapping hole*, which is stopped with clay when not in use. The viscous slag flows out over a dam, so placed as to retain the iron, but to allow the escape of the slag, which floats on the iron, as fast as it accumulates in sufficient quantity. As fresh portions of the ore, fuel, and flux are continually supplied, and the iron is withdrawn from time to time, the process goes on without interruption sometimes for several years.

The gases which issue from the mouth of the blast furnace are charged with an enormous heating power; for, beside being themselves intensely hot, they contain, even after having effected the reduction, a large proportion of combustible gases, such as carbon monoxide, carburetted hydrogen, and hydrogen. They are therefore collected at the top of the furnace by a sort of conical hood, conducted off through a pipe, and burned in suitable furnaces, the heat serving to raise the temperature of the air which feeds the furnace, and to generate steam to be used for blowing and hoisting.

Cast iron contains from 2 to 6 per cent of carbon. In *white* iron, which is hard and brittle, and of crystalline texture, the carbon seems to be mainly in combination with the iron, forming a carbide; while in *gray* iron, which is slightly malleable and of granular texture, the carbon exists chiefly as graphite mechanically disseminated through the iron. Cast iron also contains a small amount of silicon, and not infrequently manganese; it is, moreover, usually contaminated with minute quantities of sulphur and phosphorus, and other elements.

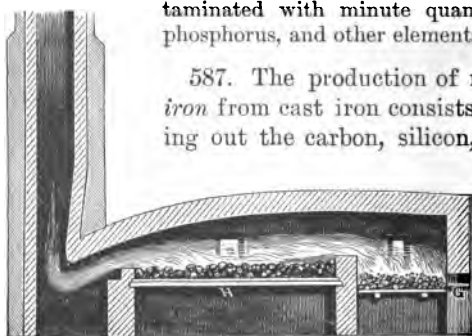


Fig. 85.

587. The production of malleable or *wrought* iron from cast iron consists essentially in burning out the carbon, silicon, sulphur, and phosphorus which cast iron contains. This oxidation of the impurities of cast iron, known as *refining*, is often effected by a process known as *pud-*

dling, which consists in melting the iron in a reverberatory

furnace, and stirring it so that the air will come in contact with it.

Fig. 85 represents a reverberatory furnace such as is used in puddling. The principle of this furnace has already been explained in § 452.

In puddling, it is customary to add to the charge of pig iron a quantity of iron scale, or other oxide of iron. The oxidation of the silicon, carbon, phosphorus, and other impurities, is effected partly by the air, but chiefly by the oxide added to the charge. When the cast iron is so far decarbonized as to be pasty in the fire, it is gathered into lumps on the end of an iron bar, and carried from the furnace to a hammer, or squeezer, which expresses the liquid slag, and welds into a coherent mass the tenacious iron. The wrought iron thus produced has a gray color, is malleable, and may be welded at a white heat. It still contains from 0.05 to 0.25 per cent of carbon.

588. Steel. — Intermediate in composition between cast and wrought iron, as far as the amount of carbon is concerned, is the invaluable substance, *steel*. It may be made from wrought iron by heating bars of iron to redness for a week or more, in contact with powdered charcoal, in close boxes from which air is carefully excluded. Though neither the iron nor the carbon fuses, yet the carbon gradually penetrates the iron, and alters its properties. In view of the recent discovery of volatile compounds of iron and carbon monoxide ($\text{Fe}(\text{CO})_4$) and of nickel and carbon monoxide ($\text{Ni}(\text{CO})_4$), it is to be inferred that in this so-called *cementation process* of steel making the carbon is carried into the iron in the form of a gas. When the bars are removed from the chests in which they were packed, it is found that the metal has become brittle and more fusible, and that it contains one to two per cent of carbon.

589. One method of making steel directly from cast iron is that known as the *Bessemer process*. A number of tons of cast iron, previously melted in a suitable furnace, are poured into a large covered crucible, called the *converter* (Fig. 86), which is made of the most refractory materials, and swung on pivots in such a manner that it can be tipped up and emptied by means of an hydraulic press. Through numerous apertures in the bottom of the crucible a blast of air is forced up into the molten metal. The combustion of the carbon and silicon of the iron, as well as of a portion of the iron itself, causes an

intense heat, which keeps the mass fluid, in spite of its rapid approach to the condition of malleable iron. Towards the end of the operation, a sufficient quantity of *spiegeleisen* is introduced into the crucible. This *spiegeleisen* is a peculiar alloy of iron, manganese, and carbon. The manganese removes some of the oxygen previously combined with iron, and some sulphur; the carbon converts the whole mass into steel, and the melted steel is immediately cast into ingots.



Fig. 86.

A modification of Bessemer's method, known as the *basic process* of Thomas and Gilchrist, permits the refining of those varieties of pig iron which are contaminated with phosphorus. To this end, the converter is lined with blocks of magnesia, and a quantity of lime is thrown in upon the surface of the molten iron, when the latter is subjected to the blast of air. The phosphorus, sulphur, and other impurities of the iron are oxidized by the air (together with some of the iron); and these oxides unite with the lime to form a cinder, or slag, which floats upon the surface of the metal. This phosphatic slag has value, since it is used in agriculture as a fertilizer. In the original Bessemer process, the converter was lined with a highly siliceous clay; but, if lime were to be heated in contact with this material, the lining would soon be destroyed by uniting with the lime to form an easily fusible slag. By these processes, steel containing any desired amount of carbon can be obtained, sufficient *spiegeleisen* being added in each instance to give the necessary amount of carbon.

The addition of a small amount of nickel, from 2 to 3 per cent, to steel confers upon it peculiar properties, especially fitting it for use as armor plate. The symbol of iron is Fe (Latin, *ferrum*).

590. Oxides and Hydroxides of Iron.—The best known of the compounds of iron and oxygen are the *monoxide* (FeO), or *ferrous oxide*, as it is often called; the *sesquioxide* (Fe_2O_3), often called *ferric oxide*; and the *ferrous ferric* or *magnetic oxide* (Fe_3O_4).

591. **Iron monoxide, or ferrous oxide (FeO)**, may be obtained by igniting ferrous oxalate in close vessels; it absorbs oxygen so rapidly that it takes fire when brought in contact with the air.

Ferrous hydroxide ($\text{Fe}(\text{OH})_2$), obtained by adding caustic alkali to a solution of a ferrous salt, is a white precipitate which rapidly changes color on exposure to the air, by taking on oxygen.

592. **Iron sesquioxide, or ferric oxide (Fe_2O_3)**, called also **red oxide of iron**, occurs abundantly in nature as hematite, specular iron, and red ocher. It is valuable as an ore of iron. It is also prepared artificially, and is much used as a pigment. A fine variety, known as *rouge*, is used for polishing glass and jewelry. By heating ferric oxide in a current of hydrogen or other reducing gas, metallic iron is readily obtained. This oxide of iron is called *sesquioxide* because it contains once and a half as many atoms of oxygen as of iron (Latin, *sesqui*, "one and a half").

Ferric hydroxide ($\text{Fe}(\text{OH})_3$) may be prepared by adding an excess of ammonia water to the solution of almost any ferric salt.

Exp. 247. — Cover a teaspoonful of fine iron filings or small tacks with 8 or 10 cc. of dilute sulphuric acid in a small bottle; when the evolution of hydrogen slackens, dilute with an equal bulk of water, and filter into a small flask. To the liquid add a few drops of strong nitric acid, and heat it to boiling. The liquor will soon be colored dark brown by the nitrous fumes resulting from the decomposition of the nitric acid, which are for a short time held dissolved by the liquid; but this deep coloration speedily passes away, and there is left only the yellowish red color of the ferric sulphate which has been formed. Add to the solution ammonia water until the odor of the latter persists, after agitation, and collect upon a filter the flocculent reddish brown precipitate of ferric hydroxide.

593. There are several ferric hydroxides which occur in nature, and differ somewhat in composition from this the normal hydroxide. Yellow ocher is a variety of ferric hydroxide. The readiness with which ferric oxide gives up oxygen to reducing agents, is shared by the hydroxides as well. The iron nails employed in the construction of ships, bridges, fences, or shoes, actually corrode, "eat up," or "burn out," the organic matter in contact with them, by absorbing oxygen from the air,

and transferring it to the carbon compound with which they are in contact. The rotting of canvas by iron rust, or of a fishing line by the rusty hook, are familiar instances of corruption by rust. Even iron itself may continue to rust inwardly when once spots of ferric hydroxide have formed upon its surface; for the hydroxide gives up some of its oxygen to the metal beneath it, and immediately takes on a new quantity from the air.

Ferric hydroxide readily absorbs hydrogen sulphide, and it is much used, on this account, in the purification of coal gas.

594. The **magnetic oxide** of iron (Fe_3O_4) occurs native. It is the richest of the ores of iron, and, when pure, contains about 72 per cent of iron. This oxide may be regarded as a compound of FeO and Fe_2O_3 , and it is sometimes called *ferrous ferric oxide*. In certain processes for producing *rustless iron*, articles are coated with this oxide by heating them in superheated steam, or in a mixture of combustible gases and air. The film of oxide thus formed protects the metal from further oxidation; for, unlike ferric oxide, the magnetic oxide does not carry in oxygen from the air to corrode the metal.

595. **Ferrates**. — A few salts called *ferrates* are known. They are analogous to manganates and chromates, and appear to be related to a ferric acid (H_2FeO_4); but neither this acid nor its anhydride (FeO_3) has been isolated.

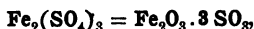
596. **Ferrous and Ferric Salts**. — There are, generally speaking, two series of iron salts, in one of which the atom **Fe** is bivalent, while in the other the atom **Fe** is probably trivalent. Thus there are two chlorides, — ferrous chloride (FeCl_2) and ferric chloride (FeCl_3): similarly, there are two nitrates, two sulphates, etc., beside many “basic salts” of the higher (ferric) oxide.

597. **Ferrous Sulphate** (FeSO_4). — A hydrate of this compound, of composition $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, usually called *copperas*, or *green vitriol*, is a cheap and abundant substance. It may readily be prepared by dissolving metallic iron or ferrous sulphide in dilute sulphuric acid. On the large scale, it is commonly prepared by roasting iron pyrites (FeS_2) at a gentle heat, and lixiviating the mixture of oxide and sulphate which is formed.

When perfectly pure, the crystals of ferrous sulphate are compact, transparent, and of a bluish green color; but in dry air they effloresce, and become covered with a white incrustation, the color of which subsequently changes to rusty brown, through absorption of oxygen. The common commercial article is of a grass-green color, and is contaminated with more or less ferric sulphate. When heated, the crystals first lose their water of crystallization; and, on further application of heat, the salt is decomposed, sulphurous and sulphuric anhydrides are given off, while ferric oxide remains. On this fact depended one method of preparing fuming sulphuric acid (§ 161). Many other ferrous salts may be produced by the solution of iron in acids.

598. **Ferric sulphate** ($\text{Fe}_2(\text{SO}_4)_3$) is interesting chiefly from its analogy with aluminum sulphate. Like the aluminum salt, it combines with the sulphates of the alkali metals to form well-defined alums.

Among many basic ferric sulphates, one known as *Monse's styptic* ($2 \text{Fe}_2\text{O}_3 \cdot 5 \text{SO}_3$) has been found useful as a means of quickly checking the bleeding of small cuts or other wounds. It is less irritating than the normal salt,



perhaps because it contains a smaller proportion of the acid.

When exposed to the air or to oxidizing agents, the ferrous salts have a great tendency to absorb oxygen.

Exp. 248. — Pour a solution of copperas into an open dish, and leave it exposed to the air for a day or two: the solution will gradually become yellow as the oxidation proceeds, and after a while a rusty precipitate of ferric oxide, or of highly basic ferric sulphate, will fall.

Exp. 249. — Dip a small piece of cotton cloth in the solution of nutgalls prepared in Exp. 186, § 420, and allow it to become dry; then dip it in the solution of copperas, and hang it up in damp air. Black, insoluble iron tannate will be so firmly precipitated in and upon the fibers of the cloth, that it cannot be washed away.

This experiment illustrates one general method of dyeing, by means of which blacks and grays of various shades may be applied to cloth or leather; though in practice other astringent dyestuffs, such as catechu, cutch, or gambier, are commonly employed in place of nutgalls.

Ferrous sulphate is largely employed in dyeing, sometimes directly, as in the foregoing experiment, but often as the source of other com-

pounds of iron, which are employed as mordants. Ferrous acetate, for example, obtained by decomposing ferrous sulphate with calcium acetate, is a compound much used by dyers. It should be remarked, however, that ferrous acetate is sometimes made directly by dissolving scraps of iron in vinegar or pyroligneous acid (§ 299). Ferrous sulphate is also used in dyeing with indigo. Its use depends upon the fact, that, when a solution of copperas is treated with calcium hydroxide, ferrous hydroxide is precipitated. This ferrous hydroxide has such a tendency to absorb oxygen, that a mixture of copperas and slaked lime forms a powerful reducing mixture.

Exp. 250. — Dissolve 1 g. of copperas (ferrous sulphate) in 100 cc. of water in a bottle of 200 cc. capacity. Into the solution stir a mixture of 1 g. of finely powdered indigo, and 1.5 g. of freshly slaked lime; fill up the bottle with water, and cork it. Shake the bottle occasionally, and, after eight or ten hours, pour off, or remove with a pipette (Appendix, § 20), a portion of the clear and nearly colorless liquid, without disturbing the precipitate in the bottom of the bottle. Expose this liquid to the air in a shallow dish. It contains white indigo in solution, but the oxygen in the air rapidly causes the formation of blue indigo, insoluble in the liquid, as was seen in Exps. 190, 191, § 430, where a different reducing agent was employed.

599. Silicates of Iron. — Several native silicates of iron are known, but none of them are of especial interest. The green tinge of ordinary glass is due to the presence of a *ferrous silicate*, and, by increasing the proportion of the ferrous salt, a deep, bottle-green color may be imparted to the glass. This color may be destroyed by introducing into the glass, during the manufacture, manganese dioxide, or some other oxidizing agent. The ferrous silicate is thus converted into *ferric silicate*, which has little coloring power.

600. Cyanides of Iron. — There is a *ferrous cyanide* ($\text{Fe}(\text{CN})_2$), known as a yellowish red precipitate, which takes up oxygen and becomes blue when exposed to the air; and a *ferric cyanide* ($\text{Fe}(\text{CN})_3$) has been obtained in solution. But by far the best known of the cyanides of iron are certain double compounds, which constitute the familiar pigments known collectively as *Prussian blue*. Common Prussian blue ($\text{Fe}_7\text{C}_{18}\text{N}_{18}$) may be regarded as a compound of ferrous and ferric cyanides, $3 \text{Fe}(\text{CN})_2 \cdot 4 \text{Fe}(\text{CN})_3$; it may be prepared as follows:—

Exp. 251. — Add to an exceedingly dilute solution of almost any ferric salt, such, for example, as the ferric sulphate of Exp. 247, § 592,

a drop of potassium ferrocyanide (§ 472). A beautiful blue precipitate will form, and will remain suspended in the liquor for a long while. Another variety of Prussian blue, known as *Turnbull's blue*, may be obtained by mixing a solution of potassium ferricyanide (§ 473) with a solution of copperas or other ferrous salt.

Since potassium ferrocyanide will give no blue coloration with ferrous salts, and since the ferricyanide yields no blue with ferric salts, it is evident that the two solutions may be used as tests by which to detect the presence of ferrous and ferric salts respectively in any solution.

Exp. 252. — Soak a piece of cotton cloth in a solution of ferric sulphate (Exp. 247, § 592), and then immerse it in an acidulated solution of potassium ferrocyanide. Prussian blue will be precipitated upon the cloth, and will remain firmly attached to it. Prussian blue is largely employed in dyeing and calico printing in a variety of ways.

601. Ferrous Sulphide (FeS) is a substance of great value to the chemist as a cheap source of the important reagent hydrogen sulphide (§ 136). The iron sulphide may be prepared by igniting pyrites in a covered crucible, by rubbing roll brimstone against a white-hot iron bar, or by fusing together sulphur and iron turnings (Exp. 69, § 134).

Exp. 253. — Dissolve a small crystal of ferrous sulphate (copperas) in water, and add to the liquid a drop or two of ammonium sulphide. Black iron sulphide will be thrown down. The finely divided ferrous sulphide thus obtained in the wet way, dissolves much more quickly in acids than the compact sulphide obtained by the way of fusion; in contact with acids, it evolves gas so tumultuously that it would be inconvenient as a source of hydrogen sulphide. The black earth between the stones of the pavements of cities, and at the bottom of drains and cesspools, owes its color to ferrous sulphide, formed by the decomposition of sulphuretted compounds in contact with ferric oxide contained in the earth.

602. Iron disulphide (FeS_2) occurs abundantly in nature as the well-known mineral iron pyrites. When this mineral is roasted at a high temperature, sulphurous anhydride is formed, and ferric oxide left, as in the manufacture of sulphuric acid. When the temperature of the burning pyrites is kept low, the product is principally ferrous sulphate; and a large amount of copperas is thus obtained by roasting pyrites, and then treating

with water. Under certain conditions, pyrites oxidizes in the air at the ordinary temperature. The spontaneous combustion of some kinds of bituminous coal is supposed to be due to the oxidation of iron pyrites disseminated through the combustible.

603. Iron carbonyl, a compound of iron and carbon monoxide, has been obtained by passing the gas over the finely divided metal. It is a gas at ordinary temperature, which is decomposed at 180° . At a low temperature, it forms an amber-colored liquid, which solidifies at -21° . It probably has the composition represented by the formula $\text{Fe}(\text{CO})_4$.

COBALT (Co), ATOMIC WEIGHT, 58.6; AND NICKEL (Ni), ATOMIC WEIGHT, 58.2.

604. Cobalt and nickel are two metals remarkably similar to each other in their physical and chemical properties. Both of them are hard, white, tenacious, and slightly magnetic. They are not tarnished by exposure to the air, and are not readily acted upon by hydrochloric or sulphuric acid, though they dissolve readily in nitric acid. They occur together in nature, generally in combination with sulphur and arsenic. Nickel is found in meteorites. They have nearly the same atomic weights, — that of nickel having been determined as 58.2, and that of cobalt as 58.6, — and nearly the same specific gravity, 8.2 to 8.9. Nickel is somewhat used as an ingredient of certain alloys, of which German silver, composed of copper, zinc, and nickel, is the most familiar.

605. Cobalt forms, with oxygen, a *monoxide* (CoO), a *sesquioxide* (Co_2O_3), and a *cobaltous cobaltic oxide* (Co_3O_4), analogous to ferrous ferric oxide. Like iron, cobalt forms two series of salts, — *cobaltous*, in which the atom is bivalent; and *cobaltic*, in which it is apparently trivalent. The cobaltous salts are well-known stable compounds; the cobaltic bodies are unstable and but little known.

Cobaltous sulphate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) is isomorphous with ferrous sulphate, and forms double salts with alkali sulphates. The crystallized salt is red.

Cobaltous chloride crystallizes from solutions in red prisms. The crystallized salt contains six molecules of water of crystal-

lization, which it readily gives up, on heating, becoming blue in color. This difference in color between the anhydrous and the hydrated salts is characteristic of cobalt salts: upon it depends their use in so-called sympathetic inks and chemical hygrometers. Cobalt is not used in the metallic state; but some of its compounds are remarkable for the beauty of their color, and find important applications in the arts. In order to give a blue color to glass or to porcelain glaze, a preparation called *smalt* is employed, which is obtained by fusing compounds of cobalt with silica and potassium carbonate, and pulverizing the resulting silicate.

606. Nickel forms but two compounds with oxygen, — a *monoxide* (NiO) and a *sesquioxide* (Ni_2O_3). The corresponding hydroxides, *nickelous hydroxide* ($\text{Ni}(\text{OH})_2$) and *nickelic hydroxide* ($\text{Ni}(\text{OH})_3$), are analogous to the hydroxides of cobalt and iron; but, unlike cobalt and iron, nickel does not form any salts in which the atom of the element is trivalent. The salts of nickel are characterized by a dark green color when crystallized. *Nickel sulphate* (NiSO_4) forms a double sulphate with ammonium.

607. Several nickel alloys are used for making coins. The five-cent pieces of the United States are made of an alloy of 25 per cent of nickel and 75 per cent of copper. The nickel coins of Germany have a similar composition. Iron is sometimes coated with a layer of nickel to prevent rusting, by placing it in a boiling solution of zinc chloride and nickel sulphate. In the process of electroplating with nickel, the object to be plated is immersed in a solution of the double sulphate of ammonium and nickel, or of the double cyanide of nickel and potassium, together with a plate of pure nickel. The plate of nickel is made the positive electrode, and, as the current from the battery or dynamo passes, electrolysis of the solution takes place, and nickel is deposited upon the object constituting the negative electrode. At the same time nickel is dissolved from the plate, and the strength of the solution is thus kept up.

608. *Nickel carbonyl* ($\text{Ni}(\text{CO})_4$) is obtained by passing carbon monoxide, at a temperature of about 30° , over finely divided nickel, or it

may be prepared by heating nickel oxalate in a stream of hydrogen at a dull red heat. At ordinary temperatures, nickel carbonyl is a colorless gas burning with a highly luminous flame. It is easily decomposed at a temperature of 200°C , pure nickel being deposited. If the gaseous body be passed through a freezing mixture, it may be condensed to a colorless liquid which solidifies at -25° , forming needle-shaped crystals.

609. Manganese, iron, nickel, and cobalt form a remarkable natural group of elements sometimes called the *iron group*. Manganese and iron, as has been seen, form similar series of salts, in one of which series the metallic atoms have a valence of two, in the other a valence of three. They both form acids of the composition H_2RO_4 , the salts of which are comparatively unstable bodies, especially in the case of the ferrates. Cobalt and nickel resemble iron in many particulars; but, while they are both capable of forming two classes of compounds, they form, by preference, those in which the atom is bivalent. Indeed, in the case of nickel, the atom is trivalent only in the sesquioxide and nickelic hydroxide ($\text{Ni}(\text{OH})_3$).

CHROMIUM (Cr).—ATOMIC WEIGHT, 51.7.

610. The chief ore of **chromium** is a compound of iron, chromium, and oxygen (FeCr_2O_4), called *chrome iron ore*. The compounds of chromium are somewhat extensively employed in the arts.

Chromium forms several oxides analogous to those of manganese, — *chromous oxide* (CrO), which is distinctly basic in its properties, yielding chromous salts; *chromium sesquioxide* (Cr_2O_3), likewise somewhat basic in character, yielding the chromic salts in which the atom of chromium is trivalent; *chromous chromic oxide* (Cr_3O_4 or $\text{CrO} \cdot \text{Cr}_2\text{O}_3$), analogous to the ferrous ferric oxide (Fe_3O_4); *chromium trioxide*, or *chromic anhydride* (CrO_3), an acidic oxide; and *perchromic acid* (Cr_2O_7).

The chromous salts are unstable. They are obtained by the reduction of the chromic compounds.

611. **Chromium sesquioxide** (Cr_2O_3), prepared by igniting the hydroxide ($\text{Cr}(\text{OH})_3$), is a green powder somewhat used as a pigment. The hydroxide may be obtained by adding ammonia water to a solution of a salt of chromium. It forms a bulky,

gelatinous, green-colored precipitate. The sesquioxide is basic in character, but, like most of the sesquioxides, does not readily afford salts of weak acids. The slightly acid character of this oxide is indicated by the existence of a few compounds derived from a hydroxide of the composition CrO_2H (chromous acid). Chrome iron ore may be regarded as such a compound; and its formula is sometimes written $(\text{CrO}_2)_2\text{Fe}$, indicating this relation, and the name *chromite of iron* has been given to it.

612. **Chromium sulphate** $(\text{Cr}_2(\text{SO}_4)_3)$ is sometimes prepared in the pure state; generally, however, it is prepared in combination with potassium (or ammonium) sulphate, forming chrome alum, a beautiful violet crystalline salt. The formula of ordinary chrome alum is $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Exp. 254. — Dissolve 15 g. of powdered potassium dichromate in 100 cc. of warm water; cool the solution, and then add to it 25 g. of concentrated sulphuric acid; cool the liquor again, and pour it into a porcelain dish, surrounded with cold water; slowly stir into the mixture 6 g. of alcohol, and set the whole aside. In the course of 24 hours the bottom of the dish will become covered with well-defined, octahedral crystals of chrome alum.

In this experiment the chromic acid which is set free by the sulphuric acid gives up a part of its oxygen to the alcohol, and is converted into chromium sulphate, which unites with the potassium sulphate to form chrome alum. The alcohol is oxidized in part to aldehyde (§ 300), the peculiar odor of which is distinctly perceived, and partly to acetic acid.

613. **Chromium trioxide, chromic oxide, or chromic anhydride** (CrO_3) , often called *chromic acid*, may be obtained by treating potassium dichromate with strong sulphuric acid. The chromic anhydride separates in red crystals, which dissolve in water, with formation of chromic acid (H_2CrO_4) .

Many chromates are known, and several of them find application in the arts. Chromium chromate $(\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3)$ is worthy of mention, because it is often regarded as chromium dioxide (CrO_2) . **Potassium dichromate** $(\text{K}_2\text{Cr}_2\text{O}_7)$, commonly known as *bichromate* or *red chromate of potash*, is the salt from which most other compounds of chromium are prepared.

Potassium dichromate is used in dyeing and calico printing, for the preparation of pigments, and in photolithography. When a mixture of gelatin and the dichromate is exposed to light, an insoluble

ble compound of gelatin and chromium oxide is formed. But from the matter thus made insoluble, any portions of the original mixture which have not been exposed to light can be washed away, and there will be left the pattern or picture which the light produced. Several chromates, notably those of lead, are valued pigments.

TUNGSTEN (W), ATOMIC WEIGHT, 182.6; **URANIUM (U)**, ATOMIC WEIGHT, 238.2; **MOLYBDENUM (Mo)**, ATOMIC WEIGHT, 95.3.

614. With chromium may be grouped *tungsten*, *uranium*, and *molybdenum*. These elements occur but sparingly in nature, and, as a rule, are comparatively unimportant. Like chromium, they all form acidic trioxides.

Tungsten trioxide forms a variety of complicated salts. A sodium compound of the formula $\text{Na}_{10}\text{W}_{12}\text{O}_4$ is used as a mordant in dyeing, and for rendering cotton and linen fabrics noninflammable. The metal itself has been used in the manufacture of tungsten steel, a small amount of it increasing the hardness of steel to a considerable extent.

Uranium forms a large number of oxides and salts. Sodium uranate ($\text{Na}_2\text{U}_2\text{O}_7$) is a fine yellow powder, which, under the name of *uranium yellow*, is used as a pigment, and for coloring glass a beautiful yellowish green. The oxide U_3O_8 is also employed in glass coloring. Uranous oxide (UO_2) gives a deep black color to glass and porcelain.

Molybdenum and its compounds are as yet of no practical use, excepting in the laboratory, where some of them are employed as important reagents.

615. **The Sesquioxide Group.**—The most striking characteristic of the principal metals which have been grouped together in this chapter is the property which they possess of forming *sesquioxides*, and various series of compounds which correspond to the sesquioxides. Most of the members of the group form monoxides as well; and if we arrange the metals in the order of their atomic weights, —

Gl (9), Al (27), Cr (51.7), Mn (55), Fe (55.6), Ni (58.2), Co (58.6), —

the sesquioxides of the metals at the head of the list are the most stable of the sesquioxides, and the monoxides of nickel and cobalt are the most stable of the monoxides, while with manganese and iron both forms of oxide are well represented. Glucinum and aluminum have no monoxides at all, and the

monoxide of chromium is very unstable. The sesquioxides and corresponding hydroxides are, as a rule, feeble bases; those of aluminum, chromium, manganese, and iron being sometimes slightly acidic also.

THE TIN GROUP.

CHAPTER XXX.

TIN, TITANIUM, GERMANIUM, ZIRCONIUM, THORIUM.

TIN (Sn). — ATOMIC WEIGHT, 118.

616. Though by no means widely diffused in nature, and though ores of it occur in but few localities, tin is one of the metals which have longest been known to man. The principal ore of tin is the dioxide, called *tinestone*. In order to extract the metal, the ore is crushed and washed to remove the lighter rock which may accompany it, and then mixed with powdered coal, and heated upon the hearth of a reverberatory furnace in a reducing flame. The reduced metal melts readily, and is run out of the furnace into iron molds. It volatilizes readily in the heat of the electric arc.

Tin is a lustrous white metal, soft, malleable, and ductile, though not very tenacious. Its ductility varies greatly with the temperature: at 100° the metal may be drawn into thin wire, but at 200° it is very brittle. When a bar of tin is bent, it emits a peculiar crackling sound, and, if the bending be repeated, the metal becomes decidedly warm. These phenomena appear to depend on the disturbance of interlaced crystals contained in the bar, and upon the friction of these crystals one against the other. Tin always exhibits a great tendency to assume the crystalline form in passing from the liquid to the solid condition. Upon this peculiarity is founded a method of ornamenting tinned iron.

Exp. 255. — Heat a piece of common tinned iron over the gas lamp until the tin has melted; thrust the plate into cold water, in order that the tin may harden quickly; then remove the smooth surface of the

metal by rubbing it, first with a bit of paper moistened with dilute aqua regia, and then with paper wet with soda lye. By this treatment there will soon be laid bare a new surface covered with beautiful crystalline figures, like frost upon a windowpane.

617. Tin does not tarnish in the air at ordinary temperatures, and for this reason, as well as on account of its brilliant luster, it is largely employed for coating other metals: copper, for example, as in ordinary pins, cooking vessels, and bath tubs; and iron, as in common tin plate, of which the so-called *tin-ware* is manufactured. *Terne plate*, used for roofing, is iron coated with an alloy of tin and lead.

618. The alloys of tin are important. The composition of bronze, bell metal, etc., has been already mentioned under copper (§ 539); and that of stereotype metal, under antimony (§ 205). Of the other alloys of tin, those formed by its union with lead are most remarkable. Plumber's solder consists commonly of equal parts of lead and tin, though some kinds of it contain only one third their weight of lead, and others only one third their weight of tin. Pewter is composed of tin, together with a small proportion of lead, and sometimes antimony.

619. **Compounds of Tin.** — There are two oxides of tin, — the *monoxide* or *stannous oxide* (SnO), and the *dioxide* or *stannic oxide* (SnO_2). The latter occurs native, and is the principal ore of tin, as already stated. A compound of the composition H_2SnO_3 may be obtained in two modifications. One form of it, obtained by treating tin with concentrated nitric acid, is insoluble in water and in acids, and is known as *metastannic acid*. With alkalis it forms salts which differ in properties and composition from the common stannates obtained from the soluble modification, which may be prepared by treating a solution of a stannate with just enough hydrochloric acid to effect its decomposition. The form thus obtained is soluble in acids, forming salts of tin, and in alkaline solutions forming stannates.

Sodium stannate ($\text{Na}_2\text{SnO}_3 \cdot 4\text{H}_2\text{O}$), prepared by deflagrating tin, niter, and caustic soda, is much used as a mordant in dyeing and calico printing. *Tin disulphide* (SnS_2), a bright, golden-yellow powder, known as *mosaic gold*, was used formerly in

decorative painting. The *chlorides* of tin (SnCl_2 and SnCl_4) are the most important of the compounds of tin, and are much used in dyeing.

Stannous chloride (SnCl_2) is a powerful reducing agent. It can change ferric salts to ferrous salts, and arsenic acid to arsenious acid. The crystallized chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) is known commercially as *tin salt*. A double soluble compound, known as *pink salt* ($2\text{NH}_4\text{Cl} \cdot \text{SnCl}_4$), is used for fixing certain dyes.

620. **Titanium (Ti)**, atomic weight 47.7; **Germanium (Ge)**, atomic weight 72; **Zirconium (Zr)**, atomic weight 90; and **Thorium (Th)**, atomic weight 231.3, — resemble tin somewhat in chemical properties. All form dioxides (RO_2), and chlorides of the composition RCl_2 and RCl_4 . Few of them are used in the arts.

GOLD, AND THE PLATINUM GROUP.

CHAPTER XXXI.

GOLD, PLATINUM, RUTHENIUM, PALLADIUM, RHODIUM, IRIDIUM, OSMIUM.

GOLD (Au). — ATOMIC WEIGHT, 196.

621. Though generally found only in small quantities, **gold** is very widely diffused upon the surface of the globe. Traces of it may be found beneath the sandy beds of most rivers, and it occurs in many of the crystalline rocks, and in the soils resulting from their decomposition. Many varieties of iron pyrites, in particular, contain appreciable quantities of gold, and silver is seldom found in nature altogether free from it. The chief source of the metal as an article of commerce is *native gold*, which is sometimes found in a condition of purity, though usually alloyed with more or less silver. It is collected either directly, by mechanically washing away the lighter substances with which it is associated, or, in the case of poorer ores, the gold is dissolved out chemically by means of quicksilver, and is subsequently recovered from the amalgam by way of distillation (§ 559).

622. Pure gold is remarkable as being the most malleable of the metals. Its softness is nearly as great as that of lead. It has, however, much tenacity, and may be drawn into extremely fine wire: 1 g. of gold can be made to yield as much as 3 km. of wire. The metal can be beaten into leaves, which are not more than $\frac{1}{10,000}$ of a millimeter thick. Thin sheets are transparent, transmitting green light. The specific gravity of gold is about 19.3.

623. In the air, gold undergoes no change at temperatures lower than its melting point; and upon this fact, taken in connection with the beautiful color and luster of the metal and its comparative rarity, its principal uses depend.

On account of this indestructibility, gold was regarded by the earlier chemists as the *king of metals*. Together with platinum and silver, it is still spoken of as a *noble metal*. Few chemical agents, excepting melted metals, have any action upon gold. None of the common acids, when taken singly, can dissolve it, though the metal is completely soluble in a mixture of hydrochloric and nitric acids (§ 83), and is not completely insoluble in nitric acid contaminated with nitrous acid or with nitrogen tetroxide. Mixtures of hydrochloric acid and various oxidizing agents, or even of this acid and ferric chloride, slowly dissolve it. The elements chlorine and bromine unite with it in the cold, and, when hot, it is attacked by phosphorus and arsenic.

624. **Alloys of Gold.**—Gold unites with most of the other metals; but its most important alloys are those with copper, silver, and mercury. Pure gold is so soft, that articles of jewelry made of it would quickly wear out if used. Such articles, as well as coins and watches, are therefore always made of gold which has been alloyed with copper, or with copper and silver, in order to increase its hardness. The standard alloy for coin in this country and in France is nine parts by weight of gold, to one part of copper; in England it is eleven parts of gold to one of copper. The composition of gold used for jewelry is usually expressed in *carats*. Pure gold is 24-carat gold; 18-carat gold contains eighteen parts of gold and six parts of copper, etc.

625. Compounds of Gold.—The compounds of gold have little chemical interest. Two oxides are known (Au_2O and Au_2O_3). They are obtained only by indirect methods, and both of them are easily decomposed by heat.

Gold Chlorides.—Gold forms three chlorides, — *aurous chloride* (AuCl), a *dichloride* (AuCl_2), and *auric chloride* (AuCl_3). Auric chloride is formed when gold is dissolved in aqua regia. It can be obtained in the form of red crystals, having the composition $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$. By contact with organic matter, it is reduced, and metallic gold is deposited in the form of a purple stain; hence its use in photography. By heating auric chloride, it is converted into aurous chloride. Auric chloride forms crystallizable double halides with the alkali chlorides; for example, AuCl_3KCl and $\text{AuCl}_3\text{NH}_4\text{Cl}$.

Auric hydroxide ($\text{Au}(\text{OH})_3$) is formed when a solution of auric chloride is treated with sodium hydroxide and then with sodium sulphate. It is easily decomposed by heat. Auric hydroxide has acidic properties. It dissolves easily in solutions of the alkali hydroxides, forming salts known as *aurates*, such as potassium aurate (KAuO_2), for example. Gold does not form salts by uniting with oxygen acids.

626. When a solution of auric chloride is treated with a mixture of dilute solutions of stannous and stannic chloride, under certain conditions, a purple-brown precipitate of uncertain composition, known as the *purple of Cassius*, is formed: this reaction is often put to use as a delicate test for the presence of gold. The purple of Cassius is employed in the arts in processes of decorating glass and porcelain.

PLATINUM (Pt).—ATOMIC WEIGHT, 193.6.

627. Platinum is a metal which, like gold, has little affinity for the other chemical elements. It is commonly found in the native state, somewhat alloyed with other metals. Like gold, it is obtained by washing away the earth and sand with which it is found mixed. It is a very heavy metal, the specific gravity of cast platinum being 21.15. The color of platinum is intermediate between the white of silver and the gray of steel; its luster is far less brilliant than that of silver. It is as soft as copper, very malleable, and very tenacious; it may

be drawn into wire so fine that its diameter is only $\frac{1}{1200}$ of a millimeter. It is not fusible in ordinary furnaces, but may be fused in the blowpipe flame, and is nowadays melted in considerable quantities in lime crucibles by means of a blowpipe flame, obtained from common coal gas and oxygen. At the high temperature of the electric arc, both platinum and gold may be volatilized.

628. Platinum does not oxidize in the air at any temperature, nor is it attacked by any of the common acids taken separately; in aqua regia (§ 83) it dissolves slowly, much less readily than gold. Chlorine water dissolves it, but neither bromine nor iodine has any action upon it. It is somewhat slowly attacked, at a red heat, by alkaline hydroxides, sulphides, and cyanides.

From its comparative inertness as a chemical agent, taken in connection with its infusibility, platinum is an extremely useful metal to the chemist. It is employed in the scientific laboratory for crucibles, evaporating dishes, stills, tubes, spatulæ, forceps, wire, blowpipe tips, and the like; and in the manufacture of oil of vitriol, large platinum stills, together with cooling siphons of the same metal, are employed in the process of concentrating the acid. Platinum expands less than any other metal when heated; and its rate of expansion so nearly resembles that of glass, that wires of platinum thrust into or through softened glass remain tightly embedded when the glass cools; hence the use of platinum in making globes for electric (incandescent) lamps, etc.

With most of the other metals platinum unites readily, forming alloys, which, in many instances, are more fusible than platinum itself: hence, in employing platinum vessels in chemical experiments, care must be taken never to touch the platinum with easily fusible metals, or to place in the vessels any easily reducible compound of a metal.

629. A remarkable property of platinum is that of inducing various gases to combine chemically one with the other. This power of causing combination is possessed even by clean surfaces of the ordinary solid metal, though to a much greater degree by spongy platinum (Exp. 258), and still more by the finely divided powder known as *platinum black*.

Exp. 256. — Cut half a gram or more of worn-out platinum foil or wire into small fragments, and boil them with a teaspoonful of aqua regia so long as the metal appears to be acted upon; then decant the liquid into a porcelain dish, add to the fragments of platinum another teaspoonful of aqua regia, and proceed as before, repeating the treatment until all the metal has dissolved. By the repeated action of successive small portions of the solvent, platinum and other comparatively insoluble substances can be dissolved much more readily than if all the liquid necessary for its solution were added at once. Evaporate the solution to dryness upon a water bath, take up the residue with water, and preserve the solution of platonic chloride (PtCl_4) thus obtained in a bottle provided with a glass stopper.

Exp. 257. — Pour a teaspoonful of a solution of ammonium chloride into a test tube, acidulate the liquid with hydrochloric acid, and add to it a drop of the solution of the platonic chloride obtained in the preceding experiment. A yellow insoluble powder will soon be precipitated. The composition of this precipitate may be represented by the formula $(\text{NH}_4)_2\text{PtCl}_6$. Repeat the experiment, and this time take enough of the platinum solution and of the ammonium chloride to make half a teaspoonful of the yellow precipitate, taking care that at last there shall be a slight excess of free ammonium chloride, rather than of platonic chloride, in the supernatant liquid. Allow the precipitate to settle, separate it from the clear liquor by decantation, and dry it partially at a gentle heat. When the precipitate has acquired the consistence of slightly moistened earth, transfer it to a cup-shaped piece of platinum foil, and heat it to redness in the gas flame as long as visible fumes of ammonium chloride continue to escape. All the chlorine, hydrogen, and nitrogen will be driven off, and there will remain upon the foil a gray, loosely coherent, spongelike mass of metallic platinum: it is called *platinum sponge*.

Exp. 258. — Hold the dry platinum sponge of Exp. 257 in a stream of hydrogen or of common illuminating gas issuing from a fine jet. The metal will soon begin to glow, and in a moment will become hot enough to inflame the mixture of air and gas in contact with it. Before friction matches were employed, this property of spongy platinum of inflaming hydrogen was sometimes made use of for striking a light. The mode of action of the platinum in this experiment is obscure: it has already been alluded to in § 150.

630. Platinum black is a term applied to metallic platinum even more finely divided than the sponge above described. Platinum black is not only capable of absorbing and storing up many times its own bulk of oxygen gas, but it is also capable of giving away this oxygen to many other substances. If

easily oxidizable liquids, such as alcohol or ether, are dropped upon platinum black which has previously been exposed to the air, the liquids will be oxidized and converted into new substances, while the powder becomes red-hot from the heat evolved during the act of oxidation.

631. Platinum forms two chlorides, *platinous chloride* (PtCl_2) and *platinic chloride* (PtCl_4), both of which form double halides with the alkali chlorides. The corresponding hydroxides are known, and, like auric hydroxide, the platinic compound has slightly acidic properties.

The salts of platinum of the oxygen acids are very unstable and but little known.

632. With platinum are classed several rare metals, which are never found except in association with platinum, and which closely resemble that metal. They are commonly called *platinum metals*, and the group may be appropriately termed the *platinum group*. The group comprises ruthenium (atomic weight, 101), rhodium (102.2), palladium (105.8), osmium (189.4), iridium (192.7), and platinum (193.6). Palladium is used to impart to brass gas fixtures a peculiar reddish tint, sometimes called *salmon bronze*. It has the property of absorbing or *occluding* many times its volume of hydrogen, apparently forming a compound (Pd_2H) which contains condensed hydrogen, and behaves much like an alloy. Iridium is used for the very hard tips of gold pens. Osmium forms, among other oxides, a volatile compound (OsO_4), the vapor of which is intensely poisonous. The metals of this group are noble metals; they withstand the action of the atmosphere; none of them are acted upon by nitric acid, though they dissolve in chlorine and in aqua regia. Their oxides part with all their oxygen when simply heated, leaving the metal behind.

CHAPTER XXXII.

ATOMIC WEIGHTS OF THE ELEMENTS.—THE PERIODIC LAW.

633. In the following list of the atomic weights the names of the elements are printed in alphabetical order for convenience of reference. The weights given are based upon the fundamental

datum that the atom of oxygen weighs 15.88 times as much as the atom of hydrogen, as has been shown by recent investigations. From this weight of oxygen, the weights of the other elements have been calculated. It will be noticed in some instances, that the weights, as here stated, differ slightly from those given on previous pages, where, for the sake of simplifying calculations, even numbers have occasionally been used instead of the more precise figures of the list.

Objections have sometimes been urged against the employment of the atom of hydrogen as the unit of atomic weight; and there are not a few chemists who would prefer that the atom of oxygen, with a weight of 16, should be adopted as the standard, to which all the other weights should be referred. In this case, the weight of the hydrogen atom becomes 1.0075, and the other weights of this table will vary proportionally.

| | Symbol. | At. Wt. | | Symbol. | At. Wt. |
|-------------------|---------|---------|-------------------------|---------|---------|
| Aluminum | Al | 27.0 | Iridium | Ir | 192.7 |
| Antimony | Sb | 119.0 | Iron | Fe | 55.6 |
| Arsenic | As | 74.4 | Lanthanum | La | 137.0 |
| Barium | Ba | 136.4 | Lead | Pb | 205.4 |
| Bismuth | Bi | 206.5 | Lithium | Li | 7.0 |
| Boron | B | 11.0 | Magnesium | Mg | 24.0 |
| Bromine | Br | 79.4 | Manganese | Mn | 55.0 |
| Cadmium | Cd | 111.4 | Mercury | Hg | 198.5 |
| Calcium | Ca | 40.0 | Molybdenum | Mo | 95.3 |
| Carbon | C | 12.0 | Neo-didymium | Ndi | 140.0 |
| Cerium | Ce | 139.0 | Nickel | Ni | 58.2 |
| Cesium | Cs | 132.0 | Nitrogen | N | 14.0 |
| Chlorine | Cl | 35.2 | Osmium | Os | 189.4 |
| Chromium | Cr | 51.7 | Oxygen | O | 15.88 |
| Cobalt | Co | 58.6 | Palladium | Pd | 105.8 |
| Columbium | Cb | 93.3 | Phosphorus | P | 30.8 |
| Copper | Cu | 63.0 | Platinum | Pt | 193.6 |
| Erbium | E | 165.0 | Potassium | K | 39.0 |
| Fluorine | F | 19.0 | Praseo-didymium | Prdi | 143.0 |
| Gallium | Ga | 69.5 | Rhodium | Rh | 102.2 |
| Germanium | Ge | 72.0 | Rubidium | Rb | 85.0 |
| Glucinum | Gl | 9.0 | Ruthenium | Ru | 101.0 |
| Gold | Au | 196.0 | Samarium | Sm | 149.0 |
| Hydrogen | H | 1.0 | Scandium | Sc | 43.7 |
| Indium | In | 113.0 | Selenium | Se | 78.4 |
| Iodine | I | 126.0 | Silicon | Si | 28.2 |

| | Symbol. | At. Wt. | | Symbol. | At. Wt. |
|---------------------|---------|---------|---------------------|---------|---------|
| Silver | Ag | 107.1 | Tin | Sn | 118.0 |
| Sodium | Na | 23.0 | Titanium | Ti | 47.7 |
| Strontium | Sr | 87.0 | Tungsten | W | 182.6 |
| Sulphur | S | 32.0 | Uranium | U | 238.2 |
| Tantalum | Ta | 181.0 | Vanadium | V | 51.0 |
| Tellurium | Te | 124.0 | Ytterbium | Yt | 171.7 |
| Terbium | Tb | 159.0 | Yttrium | Yt | 88.3 |
| Thallium | Tl | 202.7 | Zinc | Zn | 65.0 |
| Thorium | Th | 231.3 | Zirconium | Zr | 90.0 |
| Thulium | Tu | 169.7 | | | |

634. **The Periodic Law.**—From time to time many attempts have been made to arrange the elements in natural groups or series, based upon relationships which were observed to subsist between the atomic weights and the properties of the elements and their compounds. It is now very generally believed that the properties of all the elements are dependent upon the weights of their atoms much in the same way that the properties of the higher members of any homologous series (§ 279) of compound bodies are seen to be dependent upon the weights of their molecules. In some cases, indeed, the change of properties appears to depend upon the degree of polymerization, or condensation, to which the bodies have been subjected (§§ 287, 336). In the case of ozone, for example, which is a polymerized oxygen, the properties of the new body (ozone) and the molecular weight are seen to change, and to become different from those of the original oxygen, at the moment when the molecules of oxygen are condensed.

In other words, it is now recognized that the properties of all the elements are *periodic functions*¹ of the atomic weights. Not only do the properties of each element depend upon the atomic weight of that element in such wise that any change of atomic weight brings about change of properties, but it is seen to be true that the changes of properties recur in regular order, and in the same order with the increase or diminution of the atomic weights: hence it has become possible to make a general classification of the elements according to what is known as the *Periodic Law*.

635. In the table on p. 393 all the elements the atomic weights of which have been fairly well determined are arranged in several horizontal lines or *series*, according to the magnitudes of their atomic

¹ In the language of mathematics, a *function* is a quantity dependent upon some other quantity for its value; and a *periodic function* is one in which equal values recur in the same order when the value of the variable is uniformly increased or diminished. The variable in the present cases is the atomic weight, and the subject to be studied is the nature of each one of the elements.

weights; and it will be noticed that this order (of increasing atomic weight) would still be maintained, in case the several series were to be thrown into a single continuous line, by connecting the right-hand end of each series with the left-hand end, or beginning, of the series in the line next beneath it. But, on examining the single line thus constructed, it will be seen, that while the various physical and chemical properties of the elements change systematically, in passing from one element to the next, these changes are sometimes gradual, and sometimes sudden. At certain fixed points in the long line, the change of properties ceases to be gradual, and there is, as it were, a step backward, or return, very nearly to the starting point; i.e., after a period of gradual changes the character of the next element in the list is seen to resemble more or less nearly that of the element at the beginning of the series. In the words of Newlands, "The eighth element, starting from a given element, is a kind of repetition of the first, like the eighth note of an octave in music."

This periodic recurrence of properties is well shown by comparing the elements between lithium and chlorine, which fall naturally into two series, as follows, —

| | | | | | | |
|----|----|----|----|---|---|-------|
| Li | Cl | B | C | N | O | F |
| Na | Mg | Al | Si | P | S | Cl, — |

in which the properties of the members of the second or lower series are repetitions of those of the members of the first series, as has been explained already when treating of the natural groups of elements. Sulphur comes below oxygen, chlorine below fluorine, phosphorus below nitrogen, silicon below carbon, etc. So, too, while the atomic weights of the elements in either of the horizontal series, as from Li to F or from Na to Cl, increase by small though definite gradations, there is a marked periodic variation on passing from one series to the next. In the instance just cited, the atomic weights of most of the members of the second series are 16 units higher than those of the first series; and still larger differences occur in the case of some of the other series.

In consonance with the gradual changes of the atomic weights in the horizontal series, the changes of properties of members of these series are less emphatic than they are in the groups of elements given in the vertical columns of the table; but the regularity of the changes in the horizontal series may readily be exhibited by running the eye across the table on any given line, and writing down statements like the following, which relates to the specific gravity of Ag 10.5, Cd 8.6, In 7.4, Sn 7.3, Sb 6.7, Te 6.2, I 4.9. So, too, as regards the valence of the elements towards oxygen, taking the series which begins with sodium, and passing from left to right, we shall have, Na_2O , MgO ,

Al_2O_3 , SiO_2 , P_2O_5 , SO_3 , Cl_2O_7 ; and in the first series we have Li_2O , GaO , B_2O_3 , CO_2 , N_2O_5 , SO_3 , and Cl_2O_7 . Analogous relations exist in respect to other physical properties beside specific gravity, and to other chemical compounds beside oxides.

It is to be observed in the horizontal lines of the table, that while most of the elements fall naturally into several series, each of which comprises seven members, there are three instances where the series extend into an eighth group; viz., in the cases of iron and the allied metals, rubidium and its associates, and osmium and its relatives. This extension of the series to eight divisions tends to recur at alternate lines of the table; i.e., with some exceptions, every other one of the series runs into Group VIII.

The vertical columns of the table contain, as a rule, those groups of elements which are naturally allied to each other through the possession of analogous or closely related properties, and whose atomic weights increase step by step, by comparatively large degrees, as we pass down the column, as has often been insisted upon in preceding chapters of this book, such as the alkali metals, the nitrogen family, the halogens, etc. In the horizontal lines of the table, on the other hand, it will be observed that the atomic weights are nearly the same in any one of the series, and that the properties of the elements change in a somewhat different way from that noticed in the groups given in the vertical columns. Indeed, it may be said of the horizontal series, that the changes are changes in kind, rather than changes in degree. It is true, none the less, that the properties of the members of each of the horizontal series do change regularly, as has been already indicated.

It is apparent that those elements in which the chemical characters of the metals are most highly developed, and whose oxides and hydroxides are most strongly basic, are comprised in the vertical Group I., that the basic character weakens in Group II., and is still weaker in Group III., while several of the hydroxides of Group IV. are both feebly basic and feebly acidic. In Group V. the acidic character predominates, and in Groups VI. and VII. most of the hydroxides are strong acids.

It will be seen, furthermore, that the members of each of the groups given in the vertical columns of the table fall naturally into two divisions of subordinate groups, and that one of these subdivisions (a) contains only members of the odd or uneven series (1st, 3d, 5th, etc.), while the other subdivision (b) comprises the members of the 2d, 4th, 6th, etc., or even series. As a rule, each of the subordinate groups consists of elements whose properties are strikingly similar. Thus, calcium, strontium, and barium are very intimately related, and so are zinc and cadmium; while magnesium is allied to calcium in some respects, and in others it is allied to zinc; rubidium and cesium are more nearly allied to potassium than they are to sodium; and so on.

| | GROUP I. | GROUP II. | GROUP III. | GROUP IV. | GROUP V. | GROUP VI. | GROUP VII. | GROUP VIII. |
|----------------|------------------|-----------------|-----------------|-----------------|-----------------|----------------|-----------------|---|
| 1st Series... | Li 7 | Gi 9 | Bi 11 | C 12 | N 14 | O 16.88 | F 19 | |
| 2d Series... | Na 23 | Mg 24 | Al 27 | Si 28.2 | P 30.8 | S 32 | Cl 35.2 | { Fe 55.6 Ni 58.2 Co 58.6 |
| 3d Series... | K 39 | Ca 40 | Sc 43.7 | Ti 47.7 | V 51 | Cr 51.7 | Mn 55 | { Ru 101. Rh 102.2 Pd 105.8 |
| 4th Series... | (63 Cu) | 65 Zn | 69.5 Ga | 72 Ge | 74.4 As | 78.4 Se | 79.4 Br | |
| 5th Series... | Rb 85 | Sr 87 | Y 88.3 | Zr 90 | Ch 93.3 | Mo 95.3 | | |
| 6th Series... | 107.1 Ag | 111.4 Cd | 113 In | 118 Sn | 119 Sb | 124 Te | 126 I | |
| 7th Series... | Cs 132 | Ba 136.4 | La 137 | Ce 139 | Nd 140 | Pr 143 | Sm 149 | { |
| 8th Series... | | | | 150 Tb | 165 Er | | 169.7 Tu | |
| 9th Series... | | | Yb 171.7 | | Ta 181 | W 184 | | { Os 189.4 Ir 192.7 Pt 193.6 |
| 10th Series... | (196 Au) | 198.6 Hg | 202.7 Tl | 205.4 Pb | 206.5 Bi | | | |
| 11th Series... | | | | Th 231.3 | | U 238.2 | | |

One of the earliest recognitions of the existence of relations between the atomic weights and the properties of elements, was the discovery that, in many cases, where the properties of three elements are somewhat similar, the atomic weight of the middle member of the triad is usually very nearly the arithmetical mean of the atomic weights of the other two elements; thus, —

$$\text{One half of } 32 \text{ (S)} + 124 \text{ (Te)} = 78 \text{ (Se)}.$$

$$\text{One half of } 7 \text{ (Li)} + 39 \text{ (K)} = 23 \text{ (Na)}.$$

In studying this classification of the elements, it should be borne in mind that we are not yet certain as to the precise weight of the atoms of several of the elements, and that it is by no means impossible that some elements may be misplaced in the table on p. 393, because our knowledge of them is still imperfect.

636. Prediction of Elements.—It will be noticed that there are many gaps in the foregoing table which may possibly point to the existence of elements not yet discovered, whose atomic weights would properly fill the blank spaces. When the Russian chemist Mendelejeff first brought out his table, there were upon it a still larger number of gaps than we see now; for several of the blank spaces have been filled by the discovery of new elements. For example, there was a gap between calcium and titanium, and two gaps between zinc and arsenic. Mendelejeff predicted the discovery of three elements which should fill these gaps, and foretold their atomic weights and their physical and chemical properties. He gave to these supposed elements the names *eka-boron*, *eka-aluminum*, and *eka-silicon*, though when they were actually discovered they received the names *scandium*, *gallium*, and *germanium*, by which they are now known. The physical and chemical properties of the actual elements agree closely with Mendelejeff's predictions, and there was no question as to the places they should occupy in the periodic classification. Samarium, also, and other elements recently discovered, have fitted into their proper places in the system, which is now generally regarded by chemists as the expression of a fundamental law of matter.

SUPPLEMENTARY NOTES.

Note to page 14, § 11. It has been discovered that the atmosphere contains about one per cent. of an element nearly half as heavy again as nitrogen and even more inert than nitrogen. This new element exhibits so little inclination to unite with other chemical substances that it has been named argon from the Greek α privative and $\epsilon\rho\gamma\omega$, work, meaning "not working," or idle. Argon (symbol A) can be obtained in several different ways, notably as a residue by removing all the other constituents of the atmosphere. One method is to burn off the nitrogen from a quantity of air, confined over weak alkali, by gradually adding oxygen, passing a series of electric sparks, allowing the oxides of nitrogen which form to be absorbed by the alkali, and finally removing the excess of oxygen by means of pyrogallol; or, air freed from moisture and carbon dioxide may be passed through red hot copper turnings to remove oxygen, and then through a hot tube containing fragments of metallic magnesium which absorbs nitrogen and leaves the argon free.

Argon is a colorless gas 19.7 times heavier than hydrogen. There are some reasons for believing that its molecule may contain but a single atom, the weight of which would be something like 40. On the other hand, most of its properties indicate that its place in the periodic classification is between fluorine and sodium and that its atomic weight is 20. Its true position in the list of elements has not yet been definitely determined. Argon dissolves in water about two and a half times as freely as nitrogen. It can be liquefied at -121° under a pressure of 50.6 atmospheres. It solidifies at -191° , melts at -189.6° , and boils at -187° under a pressure of 740.5^{mm}. In its behavior at these low temperatures it stands between oxygen and nitrogen.

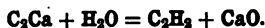
Note to page 119, § 158. The fact that sulphuric acid, unless it is highly concentrated, is apt to crystallize in cool weather compels the manufacturer to boil down his product until it has a specific gravity of at least 1.75 or 1.77 before sending it into commerce. An acid no stronger than sp. gr. 1.69 freezes readily when exposed to a moderate degree of cold, and the frozen mass would be apt to break the glass carboys in which the acid is usually transported. An incidental advantage gained by the concentration is that the strong acid becomes colorless through the oxidation and destruction of any organic matter which may have been contained in the water employed in the process of manufacture.

Note to page 133, § 175. Another method of determining molecular weight, suggested by Raoult, is specially applicable to bodies the vapor density of which cannot be ascertained. It is a matter of experience, when any substance is dissolved in a liquid capable of solidifying, that the freezing point of this liquid will be lowered in a definite degree. Moreover, — in those cases of solution where no chemical action takes place between the solvent and the body dissolved, — it appears that the freezing point is lowered by an amount proportional to the molecular weight of the dissolved substance. If then we know the molecular weight of one substance, soluble in a given liquid, and determine by experiment how much the freezing point of this liquid is lowered when a definite quantity of that substance is dissolved in a stated volume of the liquid, we can ascertain the molecular weight of another substance by determining how large an amount of it must be dissolved in a similar volume of the liquid in order to cause the same reduction of the freezing point; for in both cases the quantity of substance dissolved is proportional to the molecular weight of the substance, and the molecular weights of the two substances are related to one another in the same proportions. Thus, on dissolving one part by weight of ether ($C_4H_{10}O$) in 100 parts of water the freezing point of the liquid is reduced $0^{\circ}.23$. In order to obtain the same depression by means of glycerin, 1.24 parts of this substance will be required to the 100 parts of water. But $1 : 1.24 :: 73.88$ (Mol. Wt. Ether) : ($x = 91.61$, Mol. Wt. Glycerin). A result which consists with the formula ($C_3H_5O_3$) of glycerin.

A somewhat similar method, based on the lowering of the boiling points or *vapor tensions* of solvents by the presence of dissolved substances, is also of value.

Note to page 239, § 340. A method of obtaining acetylene from carbide of calcium yields the gas so cheaply and in such abundance that it may perhaps come into general use for purposes of illumination, as a substitute for coal gas.

Calcium carbide (C_2Ca) is prepared by heating in an electric furnace an intimate mixture of lime and carbonaceous matter, such as coal tar or powdered anthracite. It decomposes water rapidly, with development of heat and evolution of acetylene.



Diluted with air and burned in appropriate burners, the acetylene gives a flame of great illuminating power, vastly superior to the flame of coal gas.

APPENDIX.

CHEMICAL MANIPULATION.

1. **Glass Tubing.**—Two qualities of glass tubing are used in chemical experiments,—that which softens readily in the flame of a gas or spirit lamp, and that which fuses with extreme difficulty in the flame of the blast lamp. These two qualities are distinguished by the terms *soft* and *hard* glass. Soft glass may be used for all purposes, except the intense heating, or ignition, of dry substances. Fig. I. represents the most convenient sizes of glass tubing, both hard and soft, and shows also the proper thickness of the glass walls for each size.

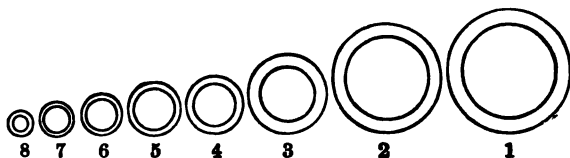


Fig. I.

2. **Cutting and Cracking Glass.**—Glass tubing and glass rod must generally be cut to the length required for any particular apparatus. A sharp triangular file is used for this purpose. The stick of tubing or rod to be cut is laid upon a table, and a deep scratch is made with the file at the place where the fracture is to be made. The stick is then grasped with the two hands, one on each side of the mark, while the thumbs are brought together just at the scratch. By pushing with the thumbs, and pulling in the opposite direction with the fingers, the stick is broken squarely at the scratch, just as a stick of candy or a dry twig may be broken. The sharp edges of the fracture should invariably be made smooth, either with a wet file, or by softening the end of the tube or rod in the lamp (Appendix, § 3). Tubes, or rods of sizes 4 to 8 inclusive may readily be cut in this manner. The larger sizes are divided with more difficulty, and it is often necessary to make

the file mark both long and deep. An even fracture is not always to be obtained with large tubes. The lower ends of glass funnels, and those ends of gas delivery tubes which enter the bottle or flask in which the gas is generated, should be filed off, or ground off on a grindstone obliquely (Fig. II.), to facilitate the dropping of liquids from such extremities.

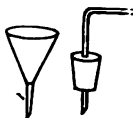


Fig. II.

In order to cut glass plates, the glazier's diamond must be resorted to. For cutting exceedingly thin glass tubes and other glass ware, like flasks, retorts, and bottles, still other means are resorted to, based upon the sudden and unequal application of heat. The process divides itself into two parts, — the producing of a crack in the required place, and the subsequent guiding of this crack in the desired direction. To produce a crack, a scratch must be made with the file, and to this scratch a pointed bit of red-hot charcoal, or the jet of flame produced by the mouth blowpipe, or a very fine gas flame, or a red-hot glass rod, may be applied. If the heat does not produce a crack, a wet stick or file may be touched upon the hot spot. Upon any part of a glass surface except the edge, it is not possible to control perfectly the direction and extent of this first crack; at an edge a small crack may be started with tolerable certainty by carrying the file mark entirely *over* the edge. To guide the crack thus started, a pointed bit of charcoal or slow match may be used. The hot point must be kept on the glass from 1 cm. to 0.5 cm. in advance of the point of the crack. The crack will follow the hot point, and may therefore be carried in any desired direction. By turning and blowing upon the coal or slow match, the point may be kept sufficiently hot. Whenever the place of experiment is supplied with common illuminating gas, a very small jet of burning gas may be advantageously substituted for the hot coal or slow match. To obtain such a sharp jet, a piece of hard-glass tube (No. 5), 10 cm. long, and drawn to a very fine point (Appendix, § 3), should be placed in the caoutchouc tube which ordinarily delivers the gas to the gas lamp, and the gas should be lighted at the fine extremity. The burning jet should have a fine point, and should not exceed 1.5 cm. in length. By a judicious use of these simple tools, broken tubes, beakers, flasks, retorts, and bottles may often be made to yield very useful articles of apparatus. No sharp edges should be allowed to remain upon glass apparatus. The durability of the apparatus itself, and of the corks and caoutchouc stoppers and tubing used with it, will be much greater, if all sharp edges are removed with the file, or, still better, rounded in the lamp.

3. Bending and Closing Glass Tubes. — Tubing of sizes 5 to 8 inclusive can generally be worked in the common gas or spirit lamp; for

larger tubes the blast lamp is necessary (Appendix, § 6). Glass tubing must not be introduced suddenly into the hottest part of the flame, lest it crack. Neither should a hot tube be taken from the flame and laid at once upon a cold surface. Gradual heating and gradual cooling are alike necessary, and are the more essential, the thicker the glass. Very thin glass will sometimes bear the most sudden changes of temperature; but thick glass, and glass of uneven thickness, absolutely require slow heating and annealing. When the end of a tube is to be heated, as in rounding sharp edges, more care is required, in consequence of the great facility with which cracks start at an edge. A tube should therefore always be brought first into the current of hot air beyond the actual flame of the gas or spirit lamp, and there thoroughly warmed, before it is introduced into the flame itself. If a blast lamp is employed, the tube may be warmed in the smoky flame, before the blast is turned on, and may subsequently be annealed in the same manner: the deposited soot will be burnt off in the first instance, and, in the last, may be wiped off when the tube is cold. In heating a tube, whether for bending, drawing, or closing, the tube must be *constantly* turned between the fingers, and also moved a little to the right and left, in order that it may be uniformly heated all around, and that the temperature of the neighboring parts may be duly raised. If a tube or rod is to be heated at any part but an end, it should be held between the thumb and first two fingers of each hand, in such a manner that the hands shall be below the tube or rod, with the palms upward, while the lamp flame is between the hands. When the end of a tube or rod is to be heated, it is best to begin by warming the tube or rod about 2 cm. from the end, and from thence to proceed slowly to the end.

The best glass will not be blackened or discolored during heating. The blackening occurs in glass which, like ordinary flint glass, contains lead (silicate). Glass containing much lead is not well adapted for chemical uses. The blackening may sometimes be removed by putting the glass in the upper or outer part of the flame, where the reducing gases are consumed, and the air has the best access to the glass. The blackening may be altogether avoided by always keeping the glass in the oxidizing part of the flame.

Glass begins to soften and bend below a visible red heat. The condition of the glass is judged of as much by the fingers as by the eye; the hands feel the yielding of the glass, either to bending, pushing, or pulling, better than the eye can see the change of color or form. It may be bent as soon as it yields in the hands, but can be drawn out only when much hotter than this. Glass tubing, however, should not be bent at too low a temperature; the curves made at too low a heat are apt to be flattened, of unequal thickness on the convex and concave sides, and brittle.

In bending tubing to make gas delivery tubes and the like, attention should be paid to the following points: (1) the glass should be equally hot on all sides; (2) it should not be twisted, pulled out, or pushed together during the heating; (3) the bore of the tube at the bend should be kept round, and not altered in size; (4) if two or more bends be made in the same piece of tubing (Fig. III., *a*), they should all be in the same plane, so that the finished tube will lie flat upon the level table.

When a tube or rod is to be bent or drawn close to its extremity, a temporary handle may be attached to it by softening the end of the tube or rod, and pressing against the soft glass a fragment of glass tube, which will adhere strongly to the softened end. The handle may subsequently be removed by a slight blow or by the aid of a file. If a considerable bend is to be made, so that the angle between the arms will be very small or nothing (as in a siphon, for example), the curvature cannot be well produced at one place in the tube, but

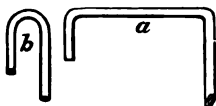


Fig. III.

should be made by heating progressively several centimeters of the tube, and bending continuously from one end of the heated portion to the other (Fig. III., *b*). Small and thick tube may be bent more sharply than large or thin tube.

In order to draw a glass tube down to a finer bore, it is simply necessary to thoroughly soften, on all sides, one or two centimeters' length of the tube, and then, taking the glass from the flame, to pull the parts asunder by a cautious movement of the hands. The larger the heated portion of glass, the longer will be the tube thus formed. Its length and fineness also increase with the rapidity of motion of the hands. If it is desirable that the finer tube should have thicker walls in proportion to its bore than the original tube, it is only necessary to keep the heated portion soft for two or three minutes before drawing out the tube, pressing the parts slightly together the while. By this process the glass will be thickened at the hot ring.

To obtain a tube closed at one end, it is best to take a piece of tubing open at both ends, and long enough to make two closed tubes. In the middle of the tube a ring of glass, as narrow as possible, must be made thoroughly soft. The hands are then separated a little, to cause a contraction in diameter at the hot and soft part. The point of the flame must now be directed, not upon the narrowest part of the tube, but upon what is to be the bottom of the closed tube. This point is indicated by the line *a* in Fig. IV. By withdrawing the right hand, the narrow part of the tube is attenuated, and finally melted off, leaving both halves of the original tube closed at one end, but not

of the same form; the right-hand half is drawn out into a long point, the other is more roundly closed. It is not possible to close handsomely the two pieces at once. The tube is seldom perfectly finished by the operation; a superfluous knob of glass generally remains upon the end. If small, it may be got rid of by heating the whole end of the tube, and blowing moderately with the mouth into the open end. The knob, being hotter, and therefore softer, than any other part, yields to the pressure from within, spreads out, and disappears. If the knob is large, it may be drawn off by sticking to it a fragment of tube, and then softening the glass above the junction. The same process may be applied to the too pointed end of the right-hand half of the original tube, or to any misshapen result of an unsuccessful attempt to close a tube, or to any bit of tube which is too short to make two closed tubes. When the closed end of a tube is too thin, it may be strengthened by keeping the whole end at a red heat for two or three minutes, turning the tube constantly between the fingers. It may be said in general, of all the preceding operations before the lamp, *that success depends on keeping the tube to be heated in constant rotation*, in order to secure a uniform temperature on all sides of the tube.



Fig. IV.

4. Blowing Bulbs, and Piercing Holes in Tubing.—If the bulb desired is large in proportion to the size of the tube on which it is to be made, the walls of the tube must be thickened by rotation in the flame of the Bunsen burner or of the blast lamp, before the bulb can be blown. If the bulb is to be blown in the middle of a piece of tubing, this thickening is effected by gently pressing the ends of the tube together while the glass is red-hot in the place where the bulb is to be. If the bulb is to be placed at the end of a tube, this end is first closed, and then suitably thickened, by keeping the closed end of the tube in the flame, and turning it continually, until enough has been accumulated at the end. The glass is then suddenly withdrawn from the flame, and the thickened portion expanded, while hot, by steadily blowing, or rather pressing, air into the tube with the mouth. The tube must be constantly turned on its axis, not only while in the flame, but also while the bulb is being blown. If too strong or too sudden a pressure be exerted with the mouth, the bulb will be extremely thin and quite useless. By watching the expanding glass, the proper moment for arresting the pressure may usually be determined. If the bulb obtained be not large enough, it may be reheated and enlarged by blowing into it again, provided that a sufficient thickness of glass remain.

It is sometimes necessary to make a hole in the side of a tube or

other thin glass apparatus. This may be done by directing a pointed flame from the blast lamp upon the place where the hole is to be, until a small spot is red-hot, and then blowing forcibly into one end of the tube, while the other end is closed by the finger. At the hot spot the glass is blown out into a thin bubble, which bursts, or may be easily broken off, leaving an aperture in the side of the tube.



Fig. V.

It is hoped that these few directions will enable the attentive student to perform sufficiently well all the manipulations with glass tubes which ordinary chemical experiments require. Much practice will alone give a perfect mastery of the details of glass blowing.

5. Lamps. — The common glass spirit lamp will be understood, without description, from the figure (Fig. V.). This lamp does not give heat enough for most ignitions; for such purposes, a lamp with circular wick, of some one of the numerous forms sold under the name of Berzelius's Argand Spirit Lamp (Fig. VI.), is necessary. These argand lamps are usually mounted on a lamp stand provided with three brass rings; but

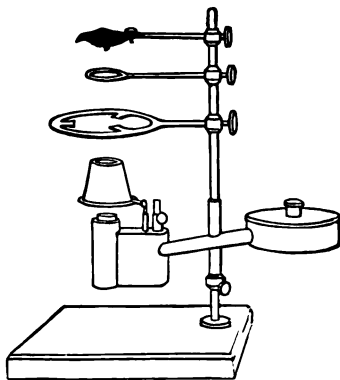


Fig. VI.

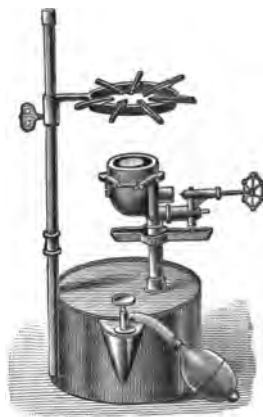


Fig. VII.

the fittings of these lamps are all made slender, in order not to carry off too much heat. When it is necessary to heat heavy vessels, other supports must be used. Dangler's laboratory lamps (Fig. VII.), burning vaporized gasolene, are valuable for use when a high temperature is desired.

Whenever gas can be obtained, gas lamps are greatly to be preferred. For all ordinary experiments, except those for which ignition tubes must be prepared, or in which considerable lengths of tubing

must be heated, the gas lamp known as Bunsen's burner will be sufficient. Fig. VIII. represents a cheap and excellent form of the Bunsen lamp. The single casting of brass, *ab*, comprises the tube *b*, through which the gas enters; and the block *a*, from which the gas escapes by two or three fine vertical holes passing through the screw *d*, and issuing from the upper face of *d*, as shown at *e*. The length of the tube *b* is 4.5 cm., and its outside diameter varies from 0.5 cm. at the outer end to 1 cm. at the junction with the block *a*. The outside diameter of the block *a* is 1.6 cm.; and its outside height, without the screws, is 1.8 cm. By the screw *c*, the piece *ab* is attached to the iron foot *g*, which may be 6 cm. in diameter.

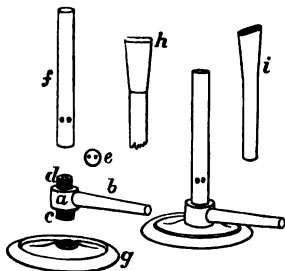


Fig. VIII.

By the screw *d*, the brass tube *f* is attached to the casting *ab*. The diameter of the face *e*, and therefore the internal diameter of the tube *f*, should be 8 mm. The length of the tube *f* is 9 cm. Through the wall of this tube, four holes 5 mm. in diameter are to be cut at such a height that the bottom of each hole will come 1 mm. above the face *e* when the tube is screwed upon *ab*. These holes are, of course, opposite each other in pairs. The finished lamp is also shown in Fig. VIII. To the tube *b* a caoutchouc tube of 5 to 7 mm. internal diameter is attached. This flexible tube should be about 1 m. long, and its other extremity should be connected with the gas cock, through the intervention of a short piece of brass gas pipe screwed into the cock. In cases where a very small flame is required, as, for instance, in evaporating small quantities of liquid, a piece of wire gauze, somewhat larger than the opening of the tube *f*, should be laid across the top of the tube, and its projecting edges pressed down tightly against the sides of the tube before the gas is lighted. In default of this precaution, the flame of a Bunsen burner, when small and exposed to currents of air, is liable to pass down the tube, and ignite the gas at *d*.

A lamp, to give a powerful flame 8 or 10 cm. long, suitable for heating tubes, may be very simply constructed by boring two holes, entering the side and issuing at the upper face, through a block of compact hard wood, 10 cm. by 6.5 cm. by 3.5 cm., and fitting short pieces of brass tubing into the holes so formed. To the tubes at the side are attached the caoutchouc tubes which deliver the gas; and from the tubes at the top, the gas issues under a sheet-iron funnel closed at the top with wire gauze. Above

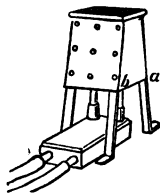


Fig. IX.

this gauze, the mixture of gas and air is to be lighted. The iron funnel will be readily understood from Fig. IX., and the following dimensions: length of the wire gauze, 10 cm.; width of the gauze, 5 cm.; width at *ab*, 9 cm.; height of the line *ab* from the table, 8.5 cm.; whole height of the funnel, 21 cm. A partition parallel to *ab* divides the funnel into two equal parts from the gauze to the level of *ab*. A long flame may also be produced with a Bunsen burner, made somewhat larger than the one described on the preceding page, and provided with a copper or brass attachment as represented in Fig. X., and by *h* in Fig. VIII. This attachment slips over the top of the tube *f* (Fig. VIII.); the flame is of the same character as that ordinarily produced, but of a different



Fig. X.

shape. Two of these lamps side by side will heat a sufficient length of glass or iron tube for all ordinary experiments.

An oil stove (Fig. XI.) is exceedingly useful in the laboratory, when large amounts of solutions are to be evaporated, or reagents made up. These baking ovens, which are sold under many forms, are useful for a variety of purposes.

6. Blast Lamps and Blowers.—For drawing, bending, and closing large glass tubes, a blast lamp is necessary. The best form is that

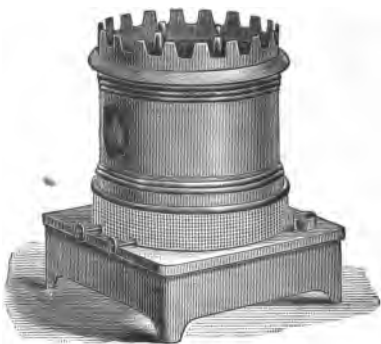


Fig. XI.

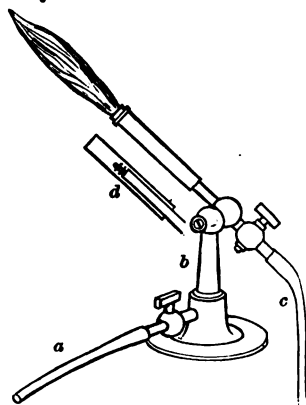


Fig. XII.

sold under the name of Bunsen's Gas Blowpipe. Its construction and the method of using it may be learned from Fig. XII.: *ab* is the pipe through which the gas enters; *c* is the tube for the blast of air; the relation of the air tube to the external gas tube is shown at *d*;

there is an outer sliding tube, by which the form and volume of the flame can be regulated.

If gas is not to be had, a lamp burning oil or naphtha must be employed. Fig. XIII. represents a glass blower's lamp made of tin, and suitable for burning oil. A large wick is essential, whether oil or naphtha be the combustible.



Fig. XIII.

For every blast lamp, a blowing machine of some sort is necessary. To supply a constant blast, it is essential that the bellows be of that construction called double, as in Fig. XIV. The bellows are made of seamless rubber cloth; the table is 0.8 m. high, from which the other dimensions may

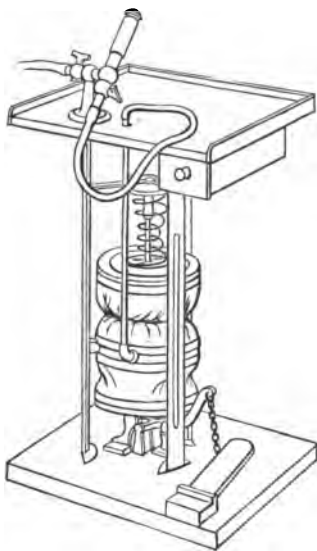


Fig. XIV.

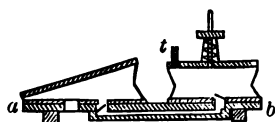


Fig. XV.

be inferred. A simpler form of bellows, and one which can be made by any carpenter or cabinet maker, is represented in perspective and in section in Fig. XV. The sides of the bellows and of the reservoir are made of stout leather. The arrangement of valves will be evident from the figure. A constant pressure is maintained on the reservoir by means of a spiral spring, and the air is delivered through the tube *t*. The rod which is represented in the figure serves simply as a guide. The entire length from *a* to *b* may be 0.6 m.

Several forms of apparatus for furnishing a blast are for sale by dealers in laboratory supplies. If there is a sufficient head of water available, the large-sized Richards's Filter Pump may be used. The accompanying figure (Fig. XVI.) shows the pump arranged to supply

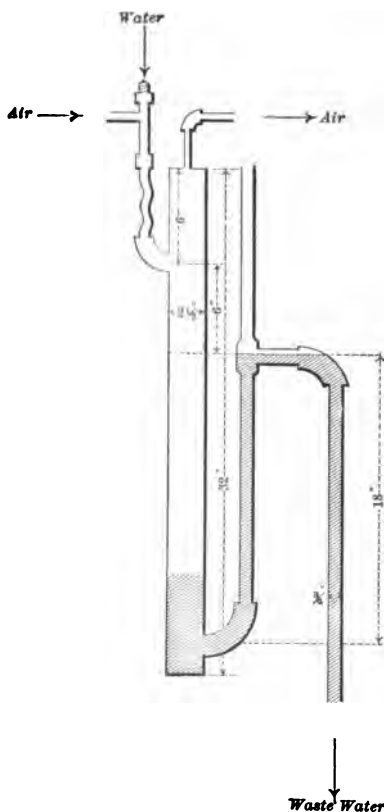


Fig. XVI.

brass or platinum. The tip should be drilled out of a solid piece of metal, and should not be fastened upon the brass tube with a screw. A trumpet-shaped mouthpiece of horn or boxwood is a convenient, though by no means essential, addition to this blowpipe. For convenience in cleaning and packing, blowpipes are often made in several pieces, as is the one represented in Fig. XVII., c.

a blast, and the dimensions of the blast attachment are given. The pump, with blast attachment, can be had of dealers in laboratory supplies.

7. **Blowpipes.** — The mouth blowpipe, in its simplest form, is a tube bent near one extremity at a right angle. Fig. XVII., a, represents a common form of blowpipe used by jewelers. The blowpipe is rendered more convenient by the addition of a mouthpiece and a chamber, near the right angle, for the condensation of moisture. Fig. XVII., b and c, represent different forms of blowpipe thus furnished. The cheapest and best form of mouth blowpipe for chemical purposes is a tube of tin plate, about 18 cm. long, 2 cm. broad at one end, and tapering to 0.7 cm. at the other (Fig. XVII., b). The broad end is closed, and serves to retain the moisture; a little above this closed end a small cylindrical tube of brass, about 5 cm. long, is soldered in at right angles; this brass tube is slightly conical at the end, and carries a small nozzle, or tip, which may be made either of

The blowpipe may be used with a candle, with gas, or with any hand lamp proper for burning oil, petroleum, or any of the so-called *burning fluids*, provided that the form of the lamp below the wick holder is such as to permit the close approach of the object to be heated to the side of the wick. When a lamp is used, a wick about 1.2 cm. long and 0.5 cm. broad is more convenient than a round or narrow wick. The wick holder should be filed off, on its longer dimension, a little obliquely, and the wick cut parallel to the holder, in order that the blowpipe flame may be directed downwards when necessary (Figs. 55, 56, § 262). A gas flame suitable for the blowpipe is readily obtained by slipping a narrow brass tube (*i*), open at both ends, into the tube *f* of Bunsen's burner (Fig. VIII.). This blowpipe tube must be long enough to close the air apertures in the tube *f*, and should be pinched together, and filed off obliquely on top. It may usually be obtained with the burner from dealers in chemical ware.

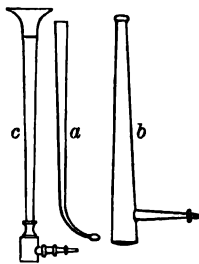


Fig. XVII.

8. **Caoutchouc.** — Vulcanized caoutchouc is a most useful substance in the laboratory, on account of its elasticity, and because it resists so well most of the corrosive substances with which the chemist deals. It is used in tubing of various diameters comparable with the sizes of glass tubing, and in stoppers of various sizes to replace corks. Caoutchouc tubing may be used to conduct all gases and liquids which do not corrode its substance, provided that the pressure under which the gas or liquid flows be not greater, or their temperature higher, than the texture of the tubing can endure. The flexibility of the tubing is a very obvious advantage in a great variety of cases. Short pieces of such tubing, a few centimeters in length, are much used, under the name of connectors, to make flexible joints in apparatus of which glass tubing forms part; flexible joints add greatly to the durability of such apparatus, because long glass tubes, bent at several angles and connected with heavy objects, like globes, bottles, or flasks full of liquid, are almost certain to break, even with the most careful usage; gas delivery tubes, and all considerable lengths of glass tubing, should invariably be divided at one or more places, and the pieces joined again with caoutchouc connectors. The ends of glass tubing to be thus connected should be squarely cut, and then rounded in the lamp, in order that no sharp edges may cut the caoutchouc. The internal diameter of the caoutchouc tube must be a little smaller than the external diameter of the glass tubes. The slipping-on of the connector is facilitated by wetting the glass.

Caoutchouc stoppers of good quality are much more durable than

corks, and are in every respect to be preferred. Caoutchouc stoppers can be bored, like corks (see next section), by means of suitable cutters, and glass tubes can be fitted into the holes thus made with a tightness unattainable with corks. Stoppers may be bought already provided with one, two, and three holes. It is not well to lay in a large stock of caoutchouc stoppers; for, though they last a long time when in constant use, they not infrequently deteriorate when kept in store, becoming hard and somewhat brittle with age.

9. **Corks.** — It is often very difficult to obtain sound, elastic corks of fine grain, and of size suitable for large flasks and wide-mouthed bottles. On this account, bottles with mouths not too large to be closed with a cork cut across the grain should be chosen for chemical uses, in preference to bottles which require large corks or bungs cut with the grain, and therefore offering continuous channels for the passage of gases, or even liquids. The kinds sold as champagne corks, and as satin corks for phials, are suitable for chemical use. The best corks generally need to be softened before using. This softening may be effected by rolling the cork under a board upon the table, or under the foot upon the clean floor, or by gently squeezing it on all sides with the well-known tool expressly adapted for this purpose, and thence called a *cork squeezer*. Steaming also softens the hardest corks.

Corks must often be cut with cleanness and precision; a sharp, thin knife, such as shoemakers use, is desirable for this purpose. When a cork has been pared down to reduce its diameter, a flat file may be employed in finishing. The file must be fine enough to leave a smooth surface upon the cork; in filing a cork, a cylindrical, not a conical, form should be aimed at.

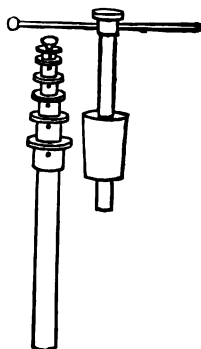


Fig. XVIII.

In boring holes through corks to receive glass tubes, a hollow cylinder of sheet brass, sharpened at one end, is a very convenient tool. Fig. XVIII. represents a set of such little cylinders of graduated sizes, slipping one within the other, into a very compact form. A stout wire, of the same length as the cylinders, accompanies the set, and serves a double purpose: passed transversely through two holes in the cap which terminates each cylinder, it gives the hand a better grasp of the tool while penetrating the cork; and when the hole is made, the wire thrust through an opening in the top of the cap expels the little cylinder of cork, which else would remain in the cutting cylinder of brass. That cutter whose diameter is next below that of the glass tube to be in-

serted in the cork is always to be selected, and, if the hole it makes is too small, a round file must be used to enlarge the aperture.

Cutters which have been dulled by use may be sharpened by filing or grinding down their outer beveled edges, and then paring off with a sharp penknife any protuberance or roughness which may remain upon the inside of the edge.

A flask which presents sharp or rough edges at the mouth can seldom be tightly corked, for the cork cannot be introduced into the neck without being cut or roughened: such sharp edges must be rounded in the lamp. In thrusting glass tubes through bored corks, the following directions are to be observed: 1. The end of the tube must not present a sharp edge capable of cutting the cork. 2. The tube should be grasped very close to the cork, in order to escape cutting the hand which holds the cork, should the tube break; by observing this precaution, the chief cause of breakage, viz., irregular lateral pressure, will be at the same time avoided. 3. A funnel tube must never be held by the funnel in driving it through a cork, nor a bent tube grasped at the bend, unless the bend comes immediately above the cork. 4. If the tube goes very hard through the cork, the application of a little soap and water will facilitate its passage; but if soap is used, the tube can seldom be withdrawn from the cork after the latter has become dry. 5. The tube must not be pushed straight into the cork, but screwed in, as it were, with a slow rotary, as well as onward motion. Joints made with corks should always be tested, before the apparatus is used, by blowing into the apparatus, and at the same time stopping up all legitimate outlets. Any leakage is revealed by the disappearance of the pressure created. To the same end, air may be sucked out of an apparatus, and its tightness proved by the permanence of the partial vacuum. To attempt to use a leaky cork is generally to waste time and labor, and to insure the failure of the experiment.

10. Iron Stand, Sand Bath, and Wire Gauze.—To support vessels over the gas lamp, an iron stand is used, consisting of a stout vertical rod fastened into a heavy, cast-iron foot, and two or more iron rings of graduated sizes, secured to the vertical rod with binding screws. All the rings may be slipped off the rod, or any ring may be adjusted at any convenient elevation. As a general rule, it is not best to apply the direct flame of the lamp to glass and porcelain vessels: hence a piece of wire gauze is stretched loosely over the largest ring, and bent downwards a little, for the reception of round-bottomed vessels; on this gauze, flasks, retorts, and porcelain dishes are usually supported. It is often a good plan to place a piece of asbestos paper

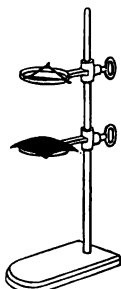


Fig. XIX.

over the wire gauze, to obtain a more equable heat. In a few cases, in which a very gradual and equable heat is required, the wire gauze is replaced by a small, shallow pan, beaten out of sheet iron, and filled with dry sand. This arrangement is called a *sand bath*. With the aid of annealed iron wire, the iron stand may be made available for

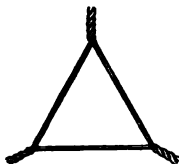


Fig. XX.

supporting tubes over the lamp. Crucibles or dishes too small for the smallest ring belonging to the stand are conveniently supported on an equilateral triangle made of three pieces of soft iron wire, twisted together at the apices, as in Fig. XX: this triangle is laid on one of the rings of the stand. An iron tripod — that is, a stout ring supported on three legs — may often be used instead of the stand above described; but it is not so generally useful, because of the difficulty of adjusting it at various heights: with a sufficiency of wooden blocks, wherewith to raise the lamp or the tripod, as occasion may require, it may be made available.

11. Pneumatic Trough. — The pneumatic trough is a contrivance which enables us to collect and confine gases in suitable vessels, and to decant them from one vessel to another. Its efficiency depends on the pressure of the atmosphere, which, as we know, is capable of supporting a column of water 10.33 m. long, or a column of mercury 76 cm. long, provided that the liquid column be so arranged that the atmospheric pressure shall be fully felt upon the foot of the column, but not at all upon its head. If a tube closed at one end and open at the other, and of any length less than 10.33 m., be completely filled with water, and then inverted, so that its open end shall dip beneath water held in a basin or saucer, the tube will remain full of water when the thumb or stopper, which closed the open end while the inversion was effected, is withdrawn. What is true of a tube is equally true of a bell, or other vessel closed at one end, of any diameter or shape, provided its height be not greater than 10.33 m.; and the principle which applies to water is equally applicable to mercury, except that the height of the mercury column, which the average atmospheric pressure can hold up, is only 76 cm., because mercury is 13.596 times heavier than water. If a few bubbles of any gas insoluble in water should be delivered beneath the open end of a tube thus standing full of water, in apparent defiance of gravitation, the gas would rise to the top of the tube by virtue of being lighter than the water, and the exact volume of water displaced by the gas, small or large, would drop into the basin or saucer beneath. If the gas were thus delivered continuously beneath the tube or bell, we should finally get the tube full of gas, without admixture of air, and sealed at the bottom by the water in the basin or saucer. If mercury were the

liquid, the operation would be precisely the same, except as regards the height of the tube. Even this difference of possible height is not noticeable in practice, because bell glasses and bottles more than 50 cm. high are very seldom used with either liquid. On account of its costliness, mercury is rarely used, unless the gas to be collected or experimented upon be soluble in water. A trough for mercury is made as small as possible, for the same reason. It is obvious that the object of a pneumatic trough may be accomplished under a great variety of forms. Any bucket or tub with a hanging shelf in it, may be made to serve. It will be sufficient to describe two convenient forms of the apparatus.

A cheap pneumatic trough is represented in Fig. XXI. It consists of two pieces: 1st, a stoneware pan, about 30 cm. in diameter on the bottom, with sides sloping slightly outwards, and rising to the height of about 10 cm. (a shallow tin pan, painted inside with asphalt paint, answers excellently for laboratory use); 2d, a deep flower-pot saucer, about 15 cm. in diameter, with one hole bored through the middle of the bottom, and a second arched hole nipped out of its rim. The saucer is inverted in the pan; in case it were to be made expressly for this purpose, it may have a height of about 5 cm., and its interior should be rounded to the hole in the center, while the outside is left flat, like the flower-pot saucer. Two blocks of wood of equal thickness, loaded with lead, or two small blocks of stone, may be used instead of the saucer. The delivery tube rests between them, and the bottle or gas cylinder is supported directly over the mouth of the delivery tube. To use this apparatus, the pan is filled with water to a level about 2 cm. above the top of the inverted saucer; the bottle, cylinder, or bell which is to receive the gas is completely filled with water from a pitcher or faucet, then closed with the hand of the operator, or with a flat piece of glass or wood, inverted into the pan, and placed on the saucer over the hole in its center: the end of the gas delivery tube is thrust through the side hole in the saucer, and the gas rising through the center hole bubbles up into the bottle or cylinder placed to receive it. While one bottle is filling with gas, another is made ready to replace it; and, when the first is full, it is pushed off the center hole of the saucer, and the second bottle is brought over the hole. A bottle full of gas may be removed from the trough by slipping beneath the mouth of the bottle a shallow plate or dish, and then lifting plate and bottle out of the pan together, in such a manner that water enough to seal the mouth of the bottle shall remain in the plate. The gas in one bottle may be



Fig. XXI.

decanted upwards into another, by filling the second bottle with water, and then carefully inclining the bottle containing the gas so as to bring its mouth under the mouth of the bottle which is full of water, keeping the mouths of both bottles all the time beneath the surface of the water in the pan. If the gas which has been collected is heavier than air, a bottle of it may be withdrawn from the water pan, and got at for use, by simply slipping a flat piece of glass or wood beneath its mouth, so as to close it rather tightly, and then standing the bottle, mouth upward, upon the table. If the cover be then removed from the bottle, the gas will not flow out, though it will slowly diffuse into the air. As the water with which the bottles or cylinders are filled falls into the pan, when displaced by gas, it is possible that the pan may become inconveniently full, if many large bottles are used: this difficulty must be remedied by dipping water out of the pan, and so restoring the true level.

Where considerable quantities of gas are frequently to be handled, and large vessels are therefore necessary, the apparatus shown in

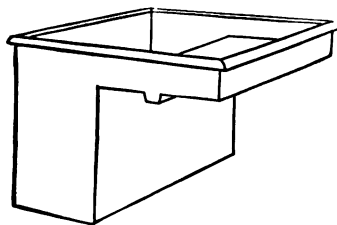


Fig. XXII.

Fig. XXII. is much more convenient than the small pan, which suffices for all common experiments. The form of this larger pneumatic trough, and the mode of using it, will readily be understood from the figure. The depth and width of the tank or well must be determined by the size of the bells and cylinders which are to be sunk in it; and the length

and breadth of the shallow part, or shelf, by the number of bells or jars of gas which are likely to be in use at any one time. The deep groove in the shelf permits a glass or caoutchouc tube to pass, without compression, under a bell whose rim projects over the groove. Such a trough is best made of wood lined with lead; zinc may be used for the lining where no acids are likely to be present. It is very convenient to have it sunk in a table, and permanently provided with a water cock and drain pipe. A chief merit of this instrument is that the glass vessels used can be filled with water by sinking them in the well much more conveniently than from a pitcher or faucet.

A pneumatic trough for mercury may be made either of wood, iron, or stone. For all common uses, it is very well cut out of a solid block of compact, hard wood, which will not split. Small cylinders or bells only can be used; and the well of the trough should be scooped out but a little larger than the bell or cylinder selected, with its principal dimension horizontal, and its bottom curved to fit the cylindrical

bell which is to be laid in it: the shelf, too, should have but a small area, sufficient only for four or five bells of 3 or 4 cm. diameter.

In using a pneumatic trough, of any construction or dimensions, the student should be on his guard against two difficulties of possible occurrence, — against the *sucking back* of the liquid in the trough into the gas-generating apparatus, and against the leakage sometimes induced by the pressure created by thrusting the gas delivery tube deep under water or mercury. The first of these difficulties is the most serious. When the flow of gas from a heated flask or tube is suddenly arrested, in consequence of some reduction of temperature, or from any other cause, it often happens that the volume of gas in the generating apparatus contracts, and the cold water or mercury from the trough rises in the delivery tube to fill the void. If the contraction is so considerable as to suffer the cold liquid to penetrate into the hot flask or tube, an explosion almost inevitably ensues, which fractures the apparatus, if it does no worse damage. In collecting over water a gas somewhat soluble in that liquid, this danger is especially imminent. The occurrence of such accidents may be effectually guarded against by paying attention to the following directions: 1. Whenever it is proposed to stop an evolution of gas which has been going on from a hot flask or tube, withdraw the delivery tube from the water *before* extinguishing the lamp, and shake off from the bent end of the tube the drops of water which are apt to adhere to it; the lamp may then be safely put out, for air can enter the apparatus through the open tube. 2. When the flow of gas from a hot apparatus is observed to slacken, watch closely the escape of the gas from the delivery tube, and as soon as any tendency to reflux of water is detected, lift the delivery tube quickly out of the water, or, better, slip off the caoutchouc connector, which should always be found between the flask and the water pan on every such piece of apparatus: if there be no connector, the cork must be loosened in the neck of the flask. Air will thus be admitted to the hot flask or tube.

These precautions apply more particularly to the cases where gas is evolved from dry materials, as in making oxygen or nitrous oxide: when a liquid is contained in the generating flask, a safety tube (Fig. 20, § 78) is a sure protection against the danger of sucking back. The atmospheric pressure can force air into a flask, in which a partial vacuum has been created, through the safety tube, by lifting and displacing a column of the liquid whose height is the length of that portion of the safety tube which dips beneath the liquid. Unless the liquid in the flask be extraordinarily dense, the force required to do this will be very much less than that required to lift a column of water whose height is determined by the elevation of the highest point of the delivery tube above the level of the water in the pan.

When the gas coming from the generating flask has to force out and keep out of the delivery tube a column of water measured from the lowest point of the tube to the surface of the water in the pan, a pressure determined by the height of this column is established upon the interior of the flask and upon every joint of the apparatus. Hence an apparatus will sometimes leak, and refuse to deliver gas at the desired point, when its delivery tube is deeply immersed, while it does not leak if the tube merely dip beneath the surface of the water. With mercury the pressure of a few centimeters is very considerable, on account of the high specific gravity of the fluid, so that this difficulty is more likely to occur with this metal than with water. Tight joints prevent the occurrence of this difficulty. A partial remedy is to dip the delivery tube as little as possible below the surface of the fluid in the trough.

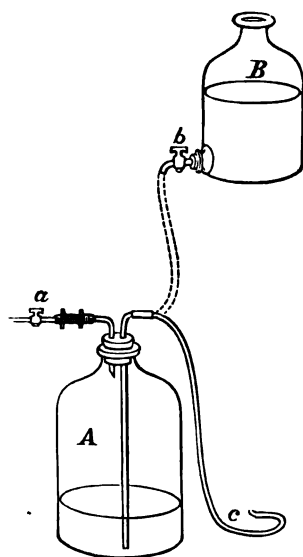


Fig. XXIII.

12. Gas Holders.—A small gas holder, very convenient for many uses, is made from a common glass bottle in the following manner: *A* (Fig. XXIII.) is a bottle of 4 to 6 l. capacity; through the cork in its neck pass two glass tubes (No. 6), of which one reaches the bottom of the bottle, while the other merely penetrates the cork; with the outer end of the first tube a caoutchouc tube (*c*) is connected, with the outer end of the second a common gas cock (*a*). The bottle being first completely filled with water, the apparatus which generates or contains the gas to be introduced into the holder is connected with the tube carrying the cock *a*: this cock is open. As the gas

presses in, the water mounts in the long tube, and flows out by the siphon *c*. In order to relieve the gas from this pressure at the beginning, it is only necessary to suck a little at *c*. The tube *c* should, of course, be thrust into a sink or drain pipe.

To get gas out of the bottle thus charged, the cock *a* is closed, and the flexible tube *c* is lifted up and connected, as shown in the figure, with a bottle of water, *B*, placed on a shelf or stand somewhat above the bottle *A*. When the cock *b* is opened, the gas in *A* is pressed upon by the weight of the superincumbent column of water, and may therefore be made to issue at will from the cock *a*. The

higher *B* is placed above *A*, the greater will be the force with which the gas will issue. If a moderate or easily regulated water pressure is at hand, supplied by city waterworks, or a reservoir in the upper part of the building, the bottle *B* is unnecessary, and the flexible tube *c* may be connected with such a water supply, whenever gas is to be pressed out of the gas holder *A*.

When larger quantities of gas are to be stored for use, a metallic gas holder, whose construction and proportions are shown in Fig. XXIV., is advantageously employed. The open cistern *B* is supported over the vessel *A* on two columns, *c*, *c*, and two tubes, *a* and *b*. Of these tubes, the first, *a*, reaches from the bottom of *B* nearly to the bottom of *A*; while the second, *b*, starts from the bottom of *B*, and just enters the arched top of *A* without projecting into it; *d* is a short, large tube, sloping upwards and outwards, and capable of being tightly closed with a cork or caoutchouc stopper; *g* is a glass gauge to show the height of the water in the vessel *A*; *e* is the discharge pipe. To fill the gas holder

with water, close *d*, open the stopcocks *a*, *b*, and *e*, and pour water into the cistern *B*; the water entering *A* will expel the air through *b* and *e*; when the water begins to flow through *e*, close that stopcock, and expel the rest of the air through *b*. The gas holder may now be filled with gas by displacing the water in the following manner: Close all the stopcocks, withdraw the cork or stopper from *d*, and introduce the tube which delivers the gas through that opening. A short piece of caoutchouc tubing makes the best end for the gas delivery tube, but glass tubing will answer the purpose if the end be slightly bent upward. The water flows out at *d* as fast as the gas enters, and the gas holder should therefore stand in a shallow metal tray provided with a drainpipe. When the desired quantity of gas has been introduced, close *d*. To draw gas out of a gas holder of this construction, the cistern *B* is filled with water, and the cork *a* is opened; under the pressure thus established, the gas may be drawn off through *e*, or allowed to rise through *b*, into bottles or bells filled with water and held over the mouth of the tube *b* in the cistern *B*; in this last case *B* answers the purpose of a pneumatic trough.

This gas holder may be cheaply made of zinc; any gas fitter can supply the necessary stopcocks. Care must be taken that the glass

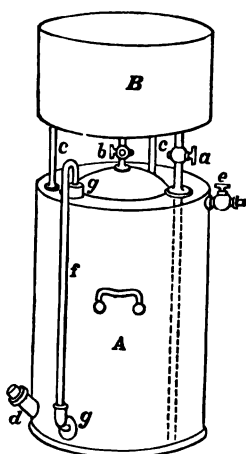


Fig. XXIV.

tube which constitutes the gauge is fitted air-tight to the gas holder. The stopcock *e* need not end in a screw; tubes may be as well connected with it by caoutchouc. The available pressure, under which the gas in the holder streams out at *e*, is of course limited by the elevation of *B* above *A*, which must always be moderate. When a stronger pressure is desirable, as in getting the oxyhydrogen blowpipe flame, for example, a heavier water column may be obtained by screwing a tall tube with a capacious funnel on top of it into the tube *a*, where it opens into the bottom of the cistern *B*. A piece of common iron or copper gas pipe, about a meter long, answers this purpose very well; the funnel at the top should hold 2 or 3 l., and must be kept full of water from a cask or tub provided with a cock and placed just above the funnel. Where a water supply, with moderate pressure, is obtainable, it may be used to keep the funnel full, or to replace the funnel altogether, if directly connected with the tube *a*. A gas holder, measuring not more than 50 cm. in total height, is not too heavy to be portable, and during the process of filling may be placed over a tub; but a gas holder of much larger proportions is better made a fixture, and provided in a permanent manner with drainpipe and water supply. The gas holder thus described is that which is the most generally useful; it may be charged from any glass flask, retort, or bottle, without any pressure being exerted upon the glass vessel; and unused gas contained in any sort of bell, bottle, or flask, can be very readily transferred to such a gas holder without waste and with very little trouble.

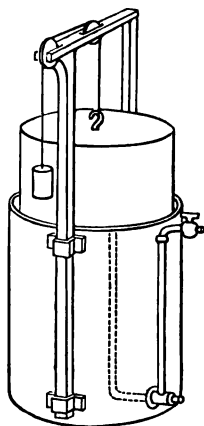


Fig. XXV.

A cheaper gas holder may be made on the plan of the large gas holders, improperly called *gasometers*, used in gas works. Fig. XXV. represents a gas holder of this sort. Over a tank of water, which may be a cylinder of zinc, as shown in the figure, or a headless pork or oil barrel, or any other water-tight tub, is balanced, by pulleys and weights, a tight bell of zinc, not too large for complete immersion in the tank. The U tube, shown in the figure, which may be either of lead or brass, serves both to introduce and deliver the gas. To fill such a gasometer, open the cock, lift the counterbalancing weight, and let the bell sink into the water; then connect the vessel from which the gas is delivered with the tube of the holder, counterpoise the bell, and the gas coming from the generator will gradually lift the bell from out the water. To force the gas out of the holder, it is only

necessary to remove the counterbalancing weight; the weight of the bell forces out the gas, and, if this pressure be not sufficient, additional weights may be placed on the top of the bell. Gas holders of this construction, unless very small, are too heavy, when filled with water, to be carried about; but this difficulty may be obviated, when economy is not specially to be regarded, by placing within the lower cylinder, or tank, a second air-tight cylinder as a core, so as to leave only a narrow space between the inner and outer cylinders for the water into which the upper bell dips. Elegant, but not cheap, gas holders are thus made, which are convenient for some uses, but are not so generally to be recommended as those of the construction first described. The vessel from which a gas holder with counterpoised bell is charged is always subjected to some pressure, slight if the pulleys, cords, and weights are in perfect order, but more frequently considerable, on account of the difficulty of maintaining such an apparatus in perfect condition.

13. Deflagrating Spoon.—The little cup which holds combustible material, to be burnt in a bottle or jar of gas, is called a *deflagrating spoon*. It may be cheaply made by hollowing a hemispherical cup out of a cube of chalk about 2 cm. on a side, and attaching a stout iron or brass wire to the chalk, in such a manner that the cup will be right side up when hung by the wire in a jar of gas: the upper end of this wire should be straight, that it may be thrust through the cork or piece of wood which covers the mouth of the bottle or jar. The piece of chalk may be replaced by a bit of the cylindrical crayons commonly used with blackboards. Brass deflagrating spoons are also to be had of philosophical-instrument makers.

14. Platinum Foil and Wire.—A piece of platinum foil, about 3 cm. square, is useful in experiments involving the evaporation of a drop or two of a liquid, or the heating of a small quantity of a solid. The foil should be at least so thick that it does not crinkle when wiped; and it is more economical to get foil which is too thick than that which is too thin, for it requires frequent cleaning. A bit of platinum wire, 0.4 mm. in diameter and 8 cm. long, will last a long time, with careful usage. No other metal, and no mixture of substances from which a metal can be reduced, must ever be heated on platinum foil or wire; for platinum forms alloys with other metals which are much more fusible than itself. If once alloyed with a baser metal, the platinum ceases to be applicable to its peculiar uses. Platinum may be cleaned by boiling it in either nitric or hydrochloric acid, by fusing the acid sulphate of sodium or potassium upon it, or by scouring it with fine sand. Aqua regia (§ 83) and chlorine water dissolve platinum; the sulphides, cyanides, and oxides of sodium and potassium, when fused in platinum vessels, slowly attack the metal.

15. Filtering.—Filtration is resorted to in order to separate a finely divided solid from a liquid. The filter may be made of paper, cloth, tow, cotton, asbestos, and other substances. Paper is the substance oftenest used. A good filtering paper must be porous enough to filter rapidly, and yet sufficiently close in texture to retain the finest powders; and it must also be strong enough to bear, when wet, the pressure of the liquid which must be poured upon it.

Filtering paper is commonly sold in sheets, which may be cut into circles of any desired diameters for use, according to the various scales of operation and quantities of liquids to be filtered; or packages of "cut filters" may be procured ready made from the dealers in chemical ware.

There are two ready methods of preparing filters for use. According to the first method, shown in Fig. XXVI., a circle of paper is folded over on its own diameter, and the semicircle thus obtained is doubled once upon itself into the form of a quadrant; the paper thus folded is opened so that three thicknesses shall come upon one side, and one thickness upon the other, as shown in the upper half of Fig. XXVI.; the filter is then placed in a glass funnel, the angle of which should be precisely that of the opened paper, viz., 60° . The paper may be so folded as to fit a funnel whose angle is more or less than 60° ; but this is the most advantageous angle, and funnels should be selected with reference to their correctness in this respect.

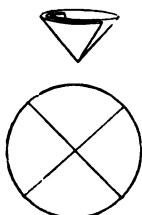


Fig. XXVI.

In the second method of folding filters, the circle of paper is doubled once upon itself, as before, into the form of a semicircle, and a fold equal to one quarter of this semicircle is turned down on each side of the paper. Each of the quarter semicircles is then folded back upon itself, as shown in the lower half of Fig. XXVII.; the filter is opened, without disturbing the folded portions, and placed in the funnel. Filtration can be rapidly effected with this kind of filter; for the projecting folds keep open passages between the filter and the funnel, and thus facilitate the passage of the liquid. That portion of the circle of paper

which must necessarily be folded up in order to give the requisite conical form to a paper filter retards filtration in the first manner of folding, but helps it in the second.

Coarse and rapid filtering can be effected with cloth bags, also by plugging the neck of a funnel loosely with tow or cotton. If a very acid or very caustic liquid, which would destroy paper, cotton, tow,

or wool, is to be filtered, the best substances wherewith to plug the neck of the funnel are asbestos and gun cotton, neither of which is attacked by such corrosive liquids.

The glass funnel which holds the filter generally requires an independent support; for it is seldom judicious or possible to support the

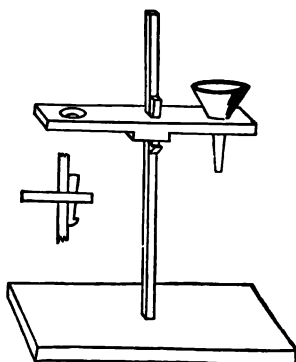


Fig. XXVIII.

funnel directly upon the vessel which receives the *filtrate*, as the clear liquid which runs through the filter is called. The iron stand (Fig. XIX.) may be used for this purpose; and wooden stands, of the form represented in Fig. XXVIII., adapted expressly for holding funnels, are very convenient, and not



Fig. XXIX.

expensive. In general, care should be taken that the lower end of the funnel touch the side or edge of the vessel into which the filtrate descends, in order that the liquid may not fall in drops, but run quietly down without splashing.

Sometimes there is no objection to thrusting a funnel directly into the neck of a bottle or flask, but in this case an ample exit for the air in the bottle must be provided (Fig. XXIX.).

16. Drying Gases.—It is often desirable to remove the aqueous vapor which is mixed with gases collected over water, or prepared from materials containing water. It very seldom happens that a gas can be prepared at one operation in so dry a state as to contain no vapor of water: this vapor must ordinarily be removed by a subsequent or additional process. Experience has shown that some gases are more easily dried than others. Ordinarily, air, hydrogen, and oxygen can be dried with ease; but there are certain other gases which can be dried only with great difficulty. Chlorine is three times as hard to dry as carbonic acid. These facts must be borne in mind in constructing and using drying apparatus. The common drying process depends upon bringing the moist gas into contact with some liquid or solid which greedily and rapidly absorbs aqueous vapor. The three substances most used for this purpose are concentrated sulphuric acid, calcium chloride, and dry quicklime. Sulphuric acid may be used in two ways: the gas may be made to bubble through a few centimeters' depth of the liquid acid, or it may be forced to pass through the interstices of a column of broken pumice stone which has been previously soaked in the acid. The latter method is the most effectual, because it

secures a more thorough contact of the gas with the hygroscopic acid than is possible during the rapid bubbling of the light gas through a shallow layer of the dense liquid. The column of fragments of pumice stone may be held in a U tube, arranged like that shown in Fig. XXX. ; but the vertical cylinder shown in the same figure is better adapted for this use, because the acid, as it becomes dilute from absorption of moisture, gradually trickles from the pumice stone, and is apt to collect in such quantity at the bottom of the U tube as to completely close the tube. In preparing the upright cylinder for use, the portion below the contraction is not filled with pumice stone; it receives the drippings from the pumice-stone column. The gas to be dried enters by the lower lateral opening, and goes out at the top of the cylinder. Though especially adapted to the column of acid-soaked pumice

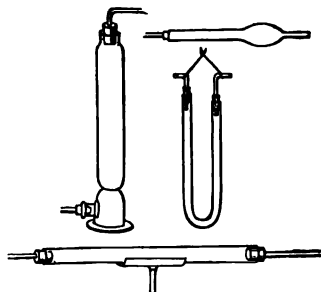


Fig. XXX.

stone, this cylinder may very well be used with either of the other drying agents, calcium chloride or quicklime. Either of the forms of drying tube represented in Fig. XXX. may be employed with these latter substances. In charging the horizontal tubes, bits of loose cotton wool should first be placed against the exit tube to prevent any particles of the calcium chloride or quicklime from entering that tube; pieces of the perfectly dry solid are then introduced in such a way that the tube

may be compactly filled with fragments, which leave room for the gas to pass very deviously between them, but offer no direct channels through which the gas could find straight and quick passage. Quicklime must be charged much more loosely than calcium chloride, because of its great expansion when moistened. Fused calcium chloride is not so well adapted for drying gases as the unfused substance. It is not at all necessary that the fragments of calcium chloride, or quicklime, should be of uniform size. When the tube is nearly full, a plug of loose cotton should be inserted before putting in the cork. A calcium chloride tube, once filled, will often serve for many experiments; whenever out of use, its outlets should be covered with paper caps; or, better, caoutchouc connectors may be slipped upon the exit tubes, and bits of glass rod thrust into these connectors. The moisture of the air is thus kept from the calcium chloride. The dimensions of drying tubes are, of course, very various. The bulb tube shown in Fig. XXX. is seldom used with a greater length than 25 cm. When this form of tube is employed, the gas should invariably enter by the end

without a cork, where the small size of the tube permits direct connection with a common gas delivery tube by means of a caoutchouc connector. The other horizontal tube, shown in the figure, may be of any length; but, whenever a great extent of drying surface is necessary, U tubes have the advantage of compactness, for many can be hung upon one short frame. The upright cylinder may be from 25 cm. to 40 cm. in height.

The choice between one or other of the three drying substances is determined, in each special case, by the chemical relations of the gas to be dried; thus, ammonia gas, which is absorbed by sulphuric acid and by calcium chloride, must be dried by passing it over quicklime, while sulphurous acid gas, which would combine with quicklime, must be dried by contact with sulphuric acid.

17. Water Bath.—It is often necessary to evaporate solutions at a moderate temperature, which can permanently be kept below a certain known limit; thus, when an aqueous solution is to be quietly evaporated, without spirting or jumping, the temperature of the solution must never be suffered to rise above the boiling point of water, nor even quite to reach this point. This quiet evaporation is best effected by the use of a water bath,—a copper cup, whose top is made of concentric rings of different diameters, to adapt it to dishes of various sizes (Fig. XXXI.). This cup, two thirds full of water, is supported on the iron stand over the lamp, and the dish containing the solution to be evaporated is placed on that one of the several rings which will permit the greater part of the dish to sink into the copper cup. The steam rising from the water impinges upon the bottom of the dish, and brings the liquid within it to a temperature which insures the evaporation of the water, but will not cause any actual ebullition. The water in the copper cup must never be allowed to boil away. Wherever a constant supply of steam is at hand, as in buildings warmed by steam, the copper cup above described may be converted into a steam bath, by attaching it to a steam pipe by means of a small tube provided with a stopcock.

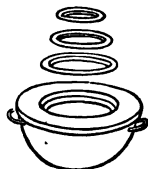


Fig. XXXI.

A cheap but serviceable water bath may be made from a quart milk can, oil can, tea canister, or any similarly shaped tin vessel, by inserting the stem of a glass funnel into the neck of the can through a well-fitting cork. In this funnel the dish containing the liquor to be evaporated rests. The can contains the water, which is to be kept just boiling. On account of the shape of the funnel, dishes of various sizes can be used with the same apparatus.

When a gradual and equable heat, higher than can be obtained upon the water bath, is required, a sand bath will sometimes be found

useful. A cheap and convenient sand bath may be made by beating a disk of thin sheet iron, about four inches in diameter, into the form of a saucer or shallow pan, and placing within it a quantity of dry sand. The dish or flask to be heated is embedded in the sand, and the apparatus placed upon a ring of the iron stand, over a gas lamp. A small tin pan answers as well for most purposes as the more expensive iron sand baths sold by the dealers in apparatus.

18. Self-regulating Gas Generator.—An apparatus which is always ready to deliver a constant stream of hydrogen, and yet does not generate the gas, except when it is immediately wanted for use, is a great convenience in an active laboratory or on a lecture table. The same remark applies to the two gases, hydrogen sulphide and carbonic acid, which are likewise used in considerable quantities, and which can

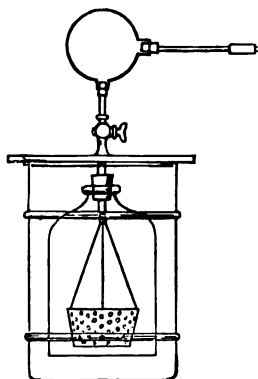


Fig. XXXII.

be conveniently generated in precisely the same form of apparatus which is advantageous for hydrogen. Such a generator may be made of divers dimensions. The following directions, with the accompanying figure (Fig. XXXII.), will enable the student to construct an apparatus of convenient size. Procure a glass cylinder 20 or 25 cm. in diameter, and 30 or 35 cm. high; ribbed candy jars are sometimes to be had of about this size. Procure also a stout tubulated bell glass, 10 or 12 cm. wide, and 5 or 7 cm. shorter than the cylinder. Get a basket of sheet lead, 7.5 cm. deep, and 2.5 cm. narrower than the bell glass, and bore a number of small holes in the sides and bottom of this basket. Cast a circular

plate of lead 7 mm. thick, and of a diameter 4 cm. larger than that of the glass cylinder; on what is intended for its under side solder three equidistant leaden strips, or a continuous ring of lead, to keep the plate in proper position as a cover for the cylinder. Fit tightly to each end of a good brass gas cock a piece of brass tube 8 cm. long, 1.5 to 2 cm. wide, and stout in metal. Perforate the center of the leaden plate, so that one of these tubes will snugly pass through the orifice, and secure it by solder, leaving 5 cm. of the tube projecting below the plate. Attach to the lower end of this tube a stout hook, on which to hang the leaden basket. By means of a sound cork and common sealing wax, or a cement made of oil mixed with red and white lead, fasten this tube into the tubulure of the bell glass, air-tight, and so firmly that the joint will bear a weight of several pounds. Hang the basket, by means of copper wire, within the bell 5 cm. above the bot-

tom of the latter. To the tube which extends above the stopcock, attach, by a good cork, the neck of a tubulated receiver of 100 or 150 cc. capacity, the interior of which has been loosely stuffed with cotton. Into the second tubulure of the receiver, fit tightly the delivery tube carrying a caoutchouc connector; into this connector can be fitted a tube adapted to convey the gas in any desired direction. This apparatus is charged by placing the zinc, iron sulphide, or marble, as the case may be, in the basket, hanging the basket in the bell, and then putting the bell glass, full of air, into its place, and closing the stopcock; the cylinder is then filled with dilute acid to within 4 cm. of the top. On opening the cock, the weight of the acid expels the air from the bell, the acid comes in contact with the solid in the basket, and a steady supply of gas is generated until either the acid is saturated or the solid dissolved. If the cock be closed, the gas accumulates in the bell, and pushes the acid below the basket, so that all action ceases. In cold weather, the apparatus must be kept in a warm place. Many forms of self-regulating gas generators can be obtained of dealers in chemical apparatus. That known as *Kipp's Generator* is excellent. For generating hydrogen, sulphuric acid diluted with four or five parts of water is used; for hydrogen sulphide, sulphuric acid is diluted with fourteen parts of water; for carbonic acid, hydrochloric acid diluted with two or three parts of water is to be preferred.

19. Glass Retorts, Flasks, Beakers, Test Tubes, Test Glasses, and Bottles. — All glass vessels which are meant for use in heating liquids must have uniformly thin bottoms. Tubulated retorts are much more generally useful than those without a tubulure; as retorts are expensive in comparison with flasks, they are less used than formerly.

The neck of a flask should have such a form that it can be tightly closed by a cork; and the lip must be strengthened to resist the force used in pressing in the cork, either by a rim of glass added on the outside, or, better, by causing the rim itself to flare outward. The actual edge of the rim must never be sharp or rough, but always smooth and rounded by partial fusion.

Beakers are thin, flat-bottomed tumblers with a slightly flaring rim. They are to be bought in sets or nests, which sometimes include a large range of sizes. The small sizes are very useful vessels; the large are so fragile as to be almost worthless. Up to the capacity of about a liter, beakers are to be recommended for heating liquids whenever it is an object to have the whole interior of the vessel readily accessible.

Test tubes are little cylinders of thin glass, with round, thin bottoms, and lips slightly flared. Their length may be from 12 cm. to 18 cm., and their diameter 1 cm. to 2 cm.; they should never have a diameter so large that the open end cannot be closed by the ball of

the thumb. To hold the tubes upright, a wooden rack is necessary; beside the row of holes to receive a dozen test tubes bottom down, the rack should have a row of pegs on which the test tubes may be inverted when not in use; in this position the water in which they are rinsed drains off, and dust cannot be deposited within the tubes. Test tubes are much used for heating small quantities of liquid over



Fig. XXXIII.

the gas or spirit lamp; they may generally be held by the upper end in the fingers without inconvenience, but if a liquid is to be boiled long in a test tube, the tube should be held in wooden nippers (Fig. 1, § 2), or in a strip of thick folded paper, nipped round the upper part of the tube, so that the two ends of the paper can be held between the thumb and forefinger just outside the tube.

The wooden nippers, above mentioned, are made of two bits of wood about a foot long, hinged together at the back, and at once connected and kept apart by a sliding steel or brass spring, somewhat like those used on certain pruning shears and some kinds of steel nippers. When a liquid is boiling actively in a test tube, it sometimes happens that portions of the hot liquid are projected out of the tube with some force. This accident may often be guarded against by holding the tube in an inclined position and continually rolling it slightly to and fro, or by moving the tube about in the flame. In any event, the operator should take care so to hold the tube that it shall not be directed either towards himself or towards any other person in his neighborhood. Test tubes are cleaned by the aid of cylindrical brushes, made of bristles caught between twisted wires, like those used for cleaning lamp chimneys: they should have a round end of bristles.

An excellent holder (see Fig. 43, § 234) is made of flexible copper or brass wire $1\frac{1}{2}$ mm. thick. This wire is twisted about a cork which serves as a handle, or, being perforated, the cork may be slipped on to the rod of a ring stand. By opening the coils at the ends more or less, it can be adapted to any test tube or ignition tube, and the tube can be supported at any angle.

Two precautions are invariably to be observed in heating test tubes: first, the outside of the tube must be wiped perfectly dry; secondly, the tube must be moved in and out of the flame for a minute or two when first heated. It should be rolled to and fro also to a slight extent between the thumb and forefinger, in order that each side of it may be equally exposed to the flame. A drop of water on the outside of the tube keeps one spot cooler than the rest. The tube breaks, because its parts, being unequally heated, expand unequally, and tear apart.

In heating glass and porcelain vessels, of whatever form, the temperature must not be raised too rapidly. When a large flask or beaker containing a cold liquid is first warmed over a lamp, moisture almost invariably condenses upon the bottom of the vessel. This moisture should be wiped off with a cloth.

Stout conical glasses, with strong stems and feet, are convenient for many uses not involving the application of heat. They are called *test glasses*, and may be had of various shapes and sizes. It is obvious that cheap wine or beer glasses and common jelly tumblers would answer the purposes which these test glasses serve.

For the collection of gases at the pneumatic trough, and for many other purposes, ordinary green glass *packing bottles* may take the place of more expensive apparatus. The smaller sizes may be conveniently used instead of beakers and test glasses, but the bottles cannot be used for the heating of liquids.

20. Pipettes. — Pipettes are tubes drawn to a point, and sometimes furnished with a bulb or a cylindrical enlargement. They are chiefly used to suck small quantities of fluid out of a vessel without disturbing the bulk of the liquid. Fig. XXXIV. represents three forms of pipette; the form with the lower end bent upwards is used to introduce liquids into a bell or bottle of gas standing over mercury. Pipettes, graduated into cubic centimeters, or holding a certain number of cubic centimeters, when filled to a mark on the stem, are often convenient.

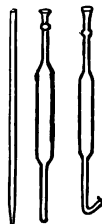


Fig. XXXIV.

Measuring glasses, divided into cubic centimeters, are made in the cylindrical form, and also in the flaring shape common in druggists' measuring glasses: the cylindrical form is to be preferred. Such a glass, of 250 cc. (or, better, of 500 cc.) capacity, is a very useful implement. Flasks holding 1 l., 500 cc., or 250 cc., when filled to a mark on the neck, are also convenient.

21. Porcelain Dishes and Crucibles. — Open dishes, which will bear heat without cracking, are necessary implements in the laboratory, for conducting the evaporation of liquids. The best evaporating dishes are those made of Berlin porcelain, glazed both inside and out, and provided with a little lip projecting beyond the rim. The dishes made of Meissen porcelain are not glazed on the outside, and are not so durable as those of Berlin manufacture; but they are much cheaper, and, with proper care, last a long time. The small Berlin dishes will generally bear an evaporation to dryness on the wire gauze over the open flame of the gas lamp; the Meissen dishes do not so well endure this severe treatment. Evaporating dishes are made of all diameters, from 3 cm. to 45 cm.; they should be ordered by specifying the diameter desired. The large sizes are expensive, and not very durable;

they should never be used except on a sand bath. Dishes of German earthenware are as good as porcelain for many uses, and are much to be recommended in place of the large sizes of porcelain dishes.

Deep porcelain dishes, provided with handles (called *casseroles*), are very useful in heating liquids which have a tendency to froth (Exps. 149, 151, §§ 317, 318), and may be obtained of various sizes. The granite and enameled ware saucepans, nowadays used for cooking purposes, are a very useful substitute for the more expensive dishes for many purposes.



Fig. XXXV.

Very thin, highly glazed porcelain crucibles, with glazed covers, are made both at Berlin and at Meissen, near Dresden; they are indispensable implements to the chemist. In general, the Meissen crucibles are thinner than the Berlin, but the Berlin crucibles are somewhat less liable to crack: both kinds are glazed inside and out, except on the outside of the bottom. Crucibles should be ordered by specifying the diameters of the sizes desired; they are to be had of nearly a dozen different sizes, with diameters varying from 2 cm. to 9 cm. The smallest and largest sizes are little used; for most purposes, the best sizes are those between 3 cm. and 5 cm. in diameter. As the covers are much less liable to be broken than the crucibles, it is advantageous to buy more crucibles than covers, whenever it is possible so to do. Porcelain crucibles are supported over the lamp on an iron-wire triangle; they must always be gradually heated, and never brought suddenly in contact with any cold substance while they are hot.

22. Rings to support Round-bottomed Vessels. — It is often necessary to support globes, round-bottomed flasks, evaporating dishes, and round receivers, in a stable manner, upon the table or other flat surface. For this purpose, rings are used, made of braided straw, or of straw wound about a core of straw, or of tin wound with listing or coarse woolen cloth. The material of which these rings are made, or with which they are covered, ought to be a substance which does not conduct heat well, because one of the chief uses of these rings is to receive hot vessels just removed from the lamp or sand bath. A hot flask or dish would almost certainly be broken, if it were placed upon the cold surface of a good conductor of heat. The student must never touch a hot vessel with cold water, or bring it into sudden contact with a surface of marble, iron, copper, or other good conductor of heat.

23. Crucibles, Furnaces, Tongs, and Iron Retort. — For preparing granulated zinc on a considerable scale, and for other purposes, the cheapest crucibles, and those which are most used, are those known as Hessian crucibles. These Hessian crucibles are sold in nests, contain-

ing from 3 to 10 crucibles. There are 10 sizes, which vary from 3 to 25 cm. in height. They generally have a triangular form, and will withstand a very high temperature, if they are warmed before being put in the fire. They are not sold with covers; but covers may be bought separately, or a triangular piece of soapstone may be very conveniently used as a cover. Crucibles are mainly used for the fusion and reduction of metals, but there are also many chemical compounds which can only be prepared at the very high temperatures which, by the use of crucibles, we are able to command. Although crucibles often withstand the most sudden changes of temperature, it is nevertheless expedient, as a general rule, to heat up a crucible gradually, and to previously warm a charge which is to be placed in a crucible already hot. If a cold crucible is to be introduced into a fire, it should first be placed in the coldest part of the fire, and gradually brought into the hottest part.

For heating these crucibles, an anthracite or coke fire in an ordinary cylinder stove will in most cases suffice. The chafing dish or open portable stove, such as is used by plumbers, for example, is very convenient for operations which require less heat. The clay buckets used as open furnaces are better than the iron ones, because they hold the heat better.

Charcoal is the fuel used in these open fires. A very useful accompaniment to these portable furnaces is a piece of straight stovepipe, about 60 cm. long and 10 cm. wide, and flaring out below like a funnel until it is wide enough to cover the top of the furnace. This contrivance powerfully increases the draught, and is used to urge the fire during kindling, or to intensify it while a fusion is in progress.

With a furnace of this description, there is no difficulty in keeping a small crucible white-hot for a short time.



Fig. XXXVI.

Small porcelain crucibles are handled, when hot, by means of small steel or iron tongs, such as are represented in Fig. XXXVI., or by means of small steel pincers, such as are used by jewelers. Larger crucibles are handled by means of tongs of various shapes and sizes, according to the weight and nature of the vessels to be lifted. Fig. XXXVII. represents two good forms of stout iron tongs for lifting large crucibles out of a coal fire. The manner of using them is readily understood from the figure.

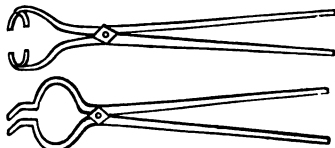


Fig. XXXVII.

A retort made of iron, of the form shown in Fig. XXXVIII., is a very convenient tool in making large quantities of oxygen, and in

preparing illuminating gas or marsh gas. The iron top is fitted to the retort, with a ground joint, fastened by a screw clamp. When the top is removed, the whole inner surface of the retort is exposed,—a decided advantage wherever the residue left in the retort after use is solid. A retort of about 300 cc. capacity is amply large for most uses. A small iron kettle makes a serviceable retort; the lid must be luted on, and the nose becomes the exit tube. A convenient and cheap retort for preparation of oxygen may be made by any tinsmith,

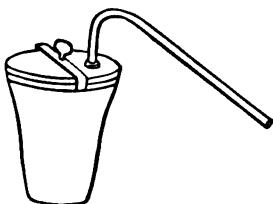


Fig. XXXVIII.

by swaging heavy sheet iron, as in the manufacture of stove-pipes, into the form of Fig. XXXIX., *a*. The mouth may be made slightly flaring, and closed with a cork carrying the delivery tube. A better

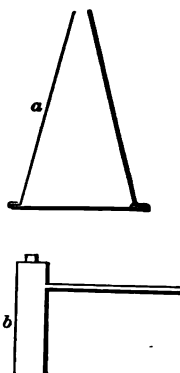


Fig. XXXIX.

plan, however, is, to provide a bit of gas piping, the interior diameter of which is such that it will slip over the mouth of the retort to the distance of an inch and a half or two inches, closed at one end, and provided with a small iron tube set into the upper portion, as shown in section in Fig. XXXIX., *b*. This may be luted upon the retort with "plaster of Paris." Before using this apparatus, all the seams should be given a coating of plaster of Paris, so as to avoid any loss of gas.

24. Mortars.—Iron, porcelain, and agate mortars are used by chemists to reduce solids to powder. An iron mortar is useful for coarse work, and for effecting the first rough breaking-up of substances which are subsequently powdered in the porcelain or agate mortar. If there be any risk of fragments being thrown out of the mortar, it should be covered with a cloth or piece of stiff paper having a hole in the middle through which the pestle may be passed. Pieces of stone, minerals, and lumps of brittle metals, may be safely broken into fragments suitable for the mortar, by wrapping them in strong paper, laying them so inclosed upon an anvil, and striking them with a heavy hammer. The paper envelope retains the broken particles, which might otherwise fly about in a dangerous manner, and be lost.

The best porcelain mortars are those known by the name of Wedgewood ware, but there are many cheaper substitutes. Porcelain mortars will not bear sharp and heavy blows; they are intended rather for grinding and trituration than for hammering. The pestle may either

be formed of one piece of porcelain, or a piece of porcelain cemented to a wooden handle; the latter is the less desirable form of pestle. Unglazed porcelain mortars are to be preferred. In selecting mortars, the following points should be attended to: 1. The mortar should not be porous; it ought not to absorb strong acids or any colored fluid, even if such liquids be allowed to stand for hours in the mortar. 2. It should be very hard, and its pestle should be of the same hardness. 3. It should be sound. 4. It should have a lip for the convenience of pouring out liquids and fine powders. As a rule, porcelain mortars will not endure sudden changes of temperature. They may be cleaned by rubbing in them a little sand soaked in nitric or sulphuric acid, or, if acids are not appropriate, in caustic soda.

Agate mortars are only intended for trituration; a blow would break them. They are exceedingly hard and impermeable. The material is so precious, and so hard to work, that agate mortars are always small. The pestles are generally inconveniently short,—a difficulty which may be remedied by fitting the agate pestle into a wooden handle.

In all grinding operations in mortars, whether of porcelain or agate, it is expedient to put only a small quantity of the substance to be powdered into the mortar at once. The operation of powdering will be facilitated by sifting the matter as fast as it is powdered, returning to the mortar the particles which are too large to pass through the sieve.

25. Spatulæ.—For transferring substances in powder, or in small grains or crystals, from one vessel to another, spatulæ and scoops made of horn or bone are convenient tools. A coarse bone paper knife makes a good spatula for laboratory use. Cards free from glaze and enamel are excellent substitutes for spatulæ.

26. Thermometers.—Thermometers intended for chemical use must have no metal, and no wood or other organic material, upon their outer surfaces; their external surfaces must be wholly of glass. The best thermometers are straight glass tubes, of uniform diameter, with cylindrical instead of spherical bulbs, and having the scale engraved upon the glass. Such instruments can be passed tightly through a cork, and are free from many liabilities to error, to which thermometers with paper or metal scales are always exposed. A cheaper kind of thermometer, having a paper scale inclosed in a glass envelope, will answer for most experiments. The Centigrade thermometer, used universally by scientific investigators, is divided into 100 degrees between the temperature at which ice melts, which is called 0°, and the temperature at which water boils, under an atmospheric pressure of 760 mm. of mercury, which is taken as 100°. A table for the conversion of degrees Centigrade to degrees of Fahrenheit's thermometer is given in § 30 of this appendix.

ORDER LIST OF CHEMICALS.

§7. The quantities here given are the approximate quantities which one person will use in performing the numbered experiments of this manual according to the directions. In ordering chemicals for a class of several students, a small reduction may be made upon the multiplied quantities. Teachers can get an idea of the cost of these chemicals by referring to the price lists and catalogues published by dealers in chemicals. The names by which the substances are known in commerce are given in the following list; such substances as sugar, starch, marble, etc., do not appear in the list:—

| | | | |
|---|---------------------|--|---------------------|
| Alcohol | 5 oz. | Copper sulphate (<i>blue vitriol</i>) | $\frac{1}{8}$ oz. |
| Alum | $\frac{1}{2}$ oz. | Ether | 1 oz. |
| Ammonia water (<i>aqua ammonia</i>) | 8 oz. | Fluor spar | $\frac{1}{2}$ oz. |
| Ammonium chloride (<i>sal ammoniac</i>) | 1 oz. | Gold leaf | 1 sq. inch |
| Ammonium nitrate | $\frac{1}{2}$ oz. | Gum arabic | $\frac{1}{2}$ oz. |
| Ammonium sulphide | $\frac{1}{2}$ oz. | Hydrochloric acid | 1 lb. |
| Anilin | $\frac{1}{8}$ oz. | Indigo | $\frac{1}{8}$ oz. |
| Anilin red | $\frac{1}{2}$ oz. | Iodine | $\frac{1}{8}$ oz. |
| Antimony, metallic | $\frac{1}{2}$ oz. | Iron (filings) | 1 oz. |
| Arsenious acid | $\frac{1}{2}$ oz. | Iron sulphate (<i>copperas</i>) | $\frac{1}{2}$ oz. |
| Barium chloride | $\frac{1}{8}$ oz. | Iron sulphide | 4 oz. |
| Benzol | $\frac{1}{2}$ oz. | Lead acetate (<i>sugar of lead</i>) | $\frac{1}{2}$ oz. |
| Bismuth, metallic | $\frac{1}{2}$ oz. | Lead nitrate | 2 oz. |
| Bleaching powder | 4 oz. | Lead oxide (<i>litharge</i>) | 2 $\frac{1}{2}$ oz. |
| Boneblack | 3 oz. | Litmus | $\frac{1}{8}$ oz. |
| Boric acid | $\frac{1}{2}$ oz. | Logwood, extract of | $\frac{1}{8}$ oz. |
| Bromine | $\frac{1}{8}$ oz. | Magnesium wire | 4 inches |
| Cadmium chloride | $\frac{1}{2}$ oz. | Manganese, black oxide of | 1 oz. |
| Calcium chloride | 1 $\frac{1}{2}$ oz. | Mercuric chloride (<i>corrosive sublimate</i>) | a few grains |
| Calcium sulphate (<i>gypsum</i>) | $\frac{1}{2}$ oz. | Mercury, red oxide of | $\frac{3}{4}$ oz. |
| Camphor | $\frac{1}{2}$ oz. | Nitric acid | 8 oz. |
| Carbolic acid, crystallized | $\frac{1}{2}$ oz. | Nitric acid, fuming | $\frac{1}{2}$ oz. |
| Carbon bisulphide | $\frac{1}{2}$ oz. | Nutgalls | $\frac{1}{2}$ oz. |
| Castor oil | 3 $\frac{1}{2}$ oz. | Oxalic acid | $\frac{1}{2}$ oz. |
| Chalk, powdered | $\frac{1}{2}$ oz. | Phosphorus | 1 oz. |
| Cochineal | $\frac{1}{8}$ oz. | Phosphorus, red | $\frac{1}{2}$ oz. |
| Copper (filings) | 2 oz. | Picric acid | $\frac{1}{8}$ oz. |
| Copper oxide | $\frac{1}{2}$ oz. | Platinum, scrap | 10 grains |

| | | | |
|--|-------------------|--------------------------------------|--------------------|
| Potassium | $\frac{1}{8}$ oz. | Sodium diborate (<i>borax</i>) . . | $\frac{1}{8}$ oz. |
| Potassium bichromate . . | 1 oz. | Sodium hydroxide (<i>caustic</i> | |
| Potassium bromide . . . | $\frac{1}{8}$ oz. | <i>soda</i>) | 3 oz. |
| Potassium carbonate, fused | $\frac{1}{8}$ oz. | Sodium hyposulphite . . | 12 oz. |
| Potassium chlorate . . . | 1 oz. | Sodium silicate, strong so- | |
| Potassium cyanide . . . | $\frac{1}{8}$ oz. | lution (<i>water glass</i>) . . | 1 oz. |
| Potassium ferrocyanide (<i>yel-</i> | | Sodium sulphate (<i>Glauber's</i> | |
| <i>low prussiate of potash</i>) . | $\frac{1}{4}$ oz. | <i>salt</i>) | 8 oz. |
| Potassium hydroxide (<i>white</i> | | Strontium nitrate . . | a few grains |
| <i>caustic potash</i>) | $\frac{1}{4}$ oz. | Sulphur, flowers of . . . | 1 oz. |
| Potassium iodide | $\frac{1}{8}$ oz. | Sulphur, roll brimstone . | 4 oz. |
| Potassium nitrate (<i>saltpeter</i>) | 3 oz. | Sulphuric acid | 2 lbs. |
| Potassium permanganate . | $\frac{3}{4}$ oz. | Tin dioxide | $\frac{1}{4}$ oz. |
| Potassium tartrate (<i>cream</i> | | Turpentine, crude . . . | $1\frac{1}{2}$ oz. |
| <i>of tartar</i>) | 1 oz. | Turpentine, oil of . . . | 4 oz. |
| Rosin | $\frac{1}{8}$ oz. | Zinc (filings or dust) . . | $\frac{1}{2}$ oz. |
| Shellac | $\frac{1}{2}$ oz. | Zinc, granulated or scraps | 2 oz. |
| Sodium | $\frac{1}{4}$ oz. | Zinc sheet, two strips 6 by 2 | |
| Sodium acetate | $\frac{1}{2}$ oz. | inches. | |
| Sodium carbonate | $\frac{1}{4}$ oz. | Zinc sulphate | $\frac{1}{2}$ oz. |

ORDER LIST OF UTENSILS.

28. The following list includes the utensils which one person will need in performing all the numbered experiments in this manual. The principal articles of steady consumption are glass tubing, retorts, flasks, corks, caoutchouc connector, and filter paper. Many of the other articles, once obtained, last a long time. It is evidently not necessary to provide all this apparatus for every member of a large class. Six retorts, as many Woulfe bottles, four soda-water bottles, two or three measuring glasses, two mortars, two pipettes, one blast lamp and bellows, three or four pieces of platinum foil, two thermometers, one pair of scales, and one set of weights, will suffice, if used with method, for a class of twenty or twenty-five students. Many of the articles can be obtained of the wholesale druggists or of dealers in hardware: for the rest, teachers can consult the priced catalogues of the dealers in philosophical apparatus and chemical wares.

Glass tubing (App. Fig. I.):—

| | |
|-----------------------------------|--|
| 1 stick about 3 ft. long of No. 1 | |
| 2 " " " " " 2 | |
| $\frac{1}{2}$ " " " " " 3 | |
| $\frac{1}{2}$ " " " " " 4 | |
| $\frac{1}{2}$ " " " " " 5 | |

2 sticks about 3 ft. long of No. 7

1 " " " " " 8

1 tube about 1 foot long and 1 inch in internal diameter.

[If ignition tubes can be bought ready made, a dozen of them may

be bought instead of one stick of No. 1 and one stick of No. 2 tubing.]

1 retort of 12 oz. capacity with glass stopper.

1 receiver of 8 or 10 oz. capacity with tubulure.

Bottles :—

1 wide-mouthed bottle, $\frac{1}{2}$ gallon.

1 “ “ “ 1 quart.

1 “ “ “ 1 pint.

2 “ “ “ 8 oz.

2 “ “ “ 4 oz.

2 “ “ “ 2 oz.

1 stout pint bottle with mouth about an inch across, for hydrogen generator.

[These bottles may be of a very common quality, such as are sold as *packing bottles*.]

Funnels :—

1 four inches in diameter.

1 two inches in diameter.

3 Woulfe bottles of about 12 oz. capacity.

Glass flasks :—

1 of 1 quart capacity.

1 of $1\frac{1}{2}$ pints' capacity.

1 of 8 oz. capacity.

2 of 4 oz. capacity.

2 of 2 oz. capacity.

1 thistle tube.

1 soda-water bottle, stout.

1 conical wineglass.

6 test tubes.

1 drying tube.

1 measuring glass of 250 cc. capacity graduated for every 10 cc.

1 measuring glass of 25 or 30 cc. capacity graduated to cubic centimeters.

1 small pipette.

1 nest of 4 or 5 beakers, of which the largest is of 250 cc. capacity.

2 or 3 bits of window glass, 3 inches square.

Porcelain evaporating dishes :—

1 about 4 inches diameter.

1 about $2\frac{1}{2}$ inches diameter.

1 deep dish (App. § 21) of 500 cc. capacity.

1 small iron mortar.

1 Wedgewood mortar about 4 inches in diameter.

1 Bunsen gas lamp with blow-pipe tube (or gasolene lamp where gas is not to be had).

1 small spirit lamp.

1 iron ring stand.

1 piece of iron wire gauze, about 4 inches square.

4 or 5 feet of stout iron wire.

4 feet iron piano wire.

1 piece fine brass (or copper) gauze, about $2\frac{1}{2}$ inches square.

2 or 3 pieces of asbestos paper, about 4 inches square.

1 iron sand bath, $4\frac{1}{2}$ inches in diameter.

1 water bath (App. § 18).

1 glass blower's lamp or Bunsen's gas blast lamp.

1 small double-acting bellows.

1 mouth blowpipe.

1 triangular and 1 round file.

1 pair jewelers' tweezers.

1 piece platinum foil, $1\frac{1}{2}$ inches square.

1 piece platinum wire, 4 inches long, and not thicker than a No. 5 needle.

1 stoneware milk pan.

1 flower-pot saucer (or two bits of wood 6 inches by 3 inches by 1 inch, loaded with lead).

1 Hessian crucible of about 8 oz. capacity.

1 lead pan for Exp. 43.

| | |
|--|--|
| 1 common plate and 1 soup plate. | Caoutchouc tubing:— |
| 1 thermometer. | 1 foot of $\frac{1}{4}$ inch. |
| 1 pair of small scales (tea scales for grocers' use). | 1 foot of $\frac{1}{8}$ inch. |
| 1 set of gram weights, 1, 2, 5, 10, 20, and 50 grams. | 4 feet of $\frac{1}{4}$ inch. |
| Corks:—An assortment of various sizes, to fit the ignition tubes, the flasks, the hydrogen generator, etc. | 1 iron spoon. |
| | 1 pair wooden nippers. |
| | 4 sheets of common filter paper, or 2 sheets of filter paper, and half a bunch of cut filters, 3 inches in diameter. |

THE METRIC SYSTEM OF WEIGHTS AND MEASURES.

29. The metric system, employed in the affairs of everyday life, by most of the nations of continental Europe, and by scientific writers throughout the world, is based upon a fundamental unit, or measure of length, called a *meter*. This meter is defined as the 40-millionth part of the circumference of the earth, or, in other words, of a "great circle," or meridian. Its length was originally determined by actual measurement of a considerable arc of a meridian, but the various measurements heretofore made of the length of the earth's meridian differ slightly from each other; and it is to be expected, and indeed hoped, that the steady improvements of methods and instruments will make each successive determination of the length of the meridian better than, and therefore different from, the preceding. It is on this account necessary to define the standard of length by legislation to be a certain rod of metal, deposited in a certain place, under specified guaranties, and to secure the uniformity and permanence of the standard by the multiplication of exact copies in safe places of deposit.

From this single quantity, the meter, all other measures are decimally derived. Multiplied or divided by 10, 100, 1000, and so forth, the meter supplies all needed linear measures; and the square meter and cubic meter, with their decimal multiples, supply all needed measures of area or surface on the one hand, and of solidity or capacity on the other.

From the unit of measure to the unit of weight, the transition is admirably simple and convenient. The cube of the one hundredth of the linear meter is, of course, the millionth of the cubic meter: its bulk is about that of a large die of the common backgammon board. This little cube of pure water is the universal unit of weight, a *gram*, which, decimally multiplied and divided, is made to express all weights. The numbers expressing all weights, from the least to the

greatest, find direct expression in the decimal notation; the weights used in different trades only differ from each other in being different decimal multiples of the same fundamental unit; and, in comparing together weights and volumes, none but easy decimal computations are ever necessary.

The nomenclature of the metrical system is extremely simple; one general principle applies to each of the following tables. The Greek prefixes for 10, 100, and 1000, viz., *deca*, *hecto*, and *kilo*, are used to signify multiplication; while the Latin prefixes for 10, 100, and 1000, viz., *deci*, *centi*, and *milli*, are employed to express subdivision. Of the names thus systematically derived from that of the unit in each table, many are not often used; the names in common use are those printed in small capitals. Thus, in the table for linear measure, only the meter, kilometer, centimeter, and millimeter are in common use, — the first for such purposes as the English yard subserves, the second instead of the English mile, the third and fourth in lieu of the fractions of the English foot and inch.

LINEAR MEASURE.

| | | Meter. | |
|-------------|--------------|--------|-----------------------------|
| Divisions . | { MILLIMETER | = | 0.001 or 1-1000 of a meter. |
| | { CENTIMETER | = | 0.01 or 1-100 “ |
| | { DECIMETER | = | 0.1 or 1-10 “ |
| Unit . . . | METER | = | 1. |
| Multiples . | { DECAMETER | = | 10. |
| | { HECTOMETER | = | 100. |
| | { KILOMETER | = | 1000. |

SURFACE MEASURE.

| | | | |
|-------------|---------------------|---|-----------------------------|
| Divisions . | { Millimeter square | = | 0.000,001 of a meter square |
| | { Centimeter square | = | 0.000,1 “ “ |
| | { Decimeter square | = | 0.01 “ “ |
| Unit . . . | METER SQUARE | = | 1. |

CUBIC MEASURE.

| | | Cubic Meter. | |
|-------------|--------------------|--------------|----------------|
| Divisions . | { Cubic Millimeter | = | 0.000,000,001 |
| | { Cubic Centimeter | = | 0.000,001 |
| | { Cubic Decimeter | = | 0.001 |
| Unit . . . | CUBIC METER | = | 1. |
| Multiples . | { Cubic Decameter | = | 1,000. |
| | { Cubic Hectometer | = | 1,000,000. |
| | { Cubic Kilometer | = | 1,000,000,000. |

The table for land measure we omit, as having no connection with our subject. For the measurement of wine, beer, oil, grain, and simi-

lar wet and dry substances, a smaller unit than the cubic meter is desirable. The cubic decimeter has been selected as a special standard of capacity for the measurement of substances, such as are bought and sold by the English wet and dry measures. The cubic decimeter (1000 cubic centimeters) thus used is called a *liter*.

CAPACITY MEASURES.

| | | Liters. | Cubic Meter. | |
|-------------|---|--------------|---------------------|----------------------|
| Divisions . | { | Milliliter = | 0.001 = 0.000,001 = | 1 cubic centimeter. |
| | | Centiliter = | 0.01 = 0.000,01 | |
| | | Deciliter = | 0.1 = 0.000,1 | |
| Unit . . | | LITER = | 1. = 0.001 | = 1 cubic decimeter. |
| Multiples . | { | Decaliter = | 10. = 0.01 | |
| | | HECTOLITER = | 100. = 0.1 | |
| | | Kiloliter = | 1,000. = 1. | = 1 cubic meter. |

The table of weights bears an intimate relation to this table of capacity. As already mentioned, the weight of that die-sized cube, a cubic centimeter, or milliliter, of distilled water (taken at 4°, its point of greatest density), constitutes the metric unit of weight. This weight is called a *gram*. From the very definition of the gram, and from the table of capacity measure, it is clear that a liter of distilled water at 4° will weigh 1,000 grams.

WEIGHTS.

| | | Grams. | |
|-------------|---|-------------|--|
| Divisions . | { | MILLIGRAM = | 0.001 |
| | | CENTIGRAM = | 0.01 |
| | | DECIGRAM = | 0.1 |
| Unit . . | | GRAM = | 1. = 1 cubic centimeter of water at 4°. |
| Multiples . | { | Decagram = | 10. |
| | | Hectogram = | 100. |
| | | Kilogram = | 1,000. = 1 cubic decimeter of water at 4°. |

The simplicity and directness of the relations between weights and volumes in the metric system can now be more fully explained. The chemist ordinarily uses the gram as his unit weight, and, for his unit of volume, a cubic centimeter, which is the bulk of a gram of water. For coarser work, the kilogram becomes the unit of weight, and the corresponding unit of measure is the liter, which is the bulk of a kilogram of water. In commercial dealings, in manufacturing processes, and, above all, in scientific investigations, these simple relations between weights and measures have been found to be an inestimable advantage. The numerical expressions for metric

weights and measures may always be read as decimals. Thus, 5.126 meters will be read, "five meters and one hundred and twenty-six thousandths," and not "five meters, one decimeter, two centimeters, and six millimeters." The expression "10.5 grams" is read "ten and five tenths grams;" just as we say one hundred and five dollars, not ten eagles and five dollars; or sixty-five cents, not six dimes and five cents. All computations under the metric system are made with decimals alone.

The abbreviations commonly met with in chemical literature are:—

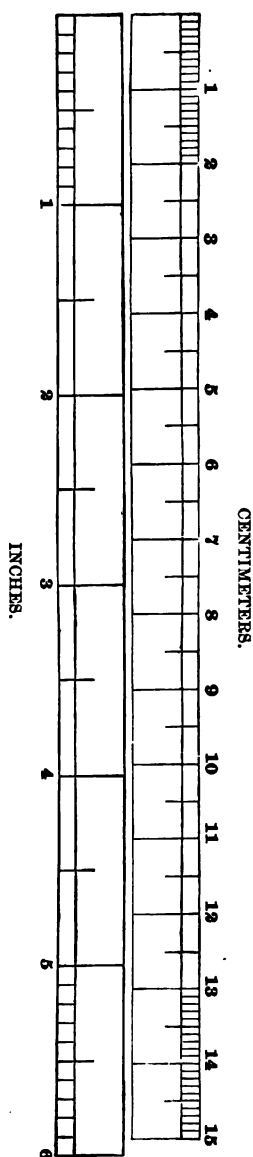
| | |
|----------------------|--|
| mm. for millimeter. | cm. for centimeter. |
| m. for meter. | cc. or cm^3 for cubic centimeter. |
| g. or grm. for gram. | k. or kgm. or kilo. for kilogram. |
| l. for liter. | |

The equivalents in English weights and measures, of those metric weights and measures which are used in chemistry, can be readily found by the aid of the table on the following page, which is available not only for grams, centimeters, and liters, but, by mere change of the position of the decimal point, for all decimal multiples or subdivisions of these quantities.

| | | |
|-------------------------------|-------------------|--------------------------|
| One cubic meter | = | 35.31660 cubic feet. |
| One cubic decimeter (a liter) | = | 61.02709 cubic inches. |
| One cubic centimeter | = | 0.06103 cubic inch. |
| One liter | = | 0.22017 imperial gallon. |
| One liter | = | 0.88066 imperial quart. |
| One liter | = | 1.76133 imperial pint. |
| One liter | = | 0.26427 U. S. gallon. |
| One liter | = | 1.05708 U. S. quart. |
| One liter | = | 2.11415 U. S. pints. |
| One gram | = | 15.4323 grains. |
| One meter | = | 39.3708 inches. |
| One pound Avoirdupois | = 7,000 | grains = 453.59 g. |
| One pound Troy | = 5,760 | grains = 373.24 g. |
| One ounce Avoirdupois | = 437.5 | grains = 28.35 g. |
| One ounce Troy | = 480 | grains = 31.10 g. |
| One grain | | = 64.80 mg. |
| One English imperial gallon | = 277.274 cu. in. | = 4.54 l. |
| One U. S. standard gallon | = 231 cu. in. | = 3.78 l. |
| One U. S. quart | | = 0.95 l. |
| One fluid ounce | | = 29.56 cc. |
| One foot | | = 0.3048 m. |
| One yard | | = 0.9144 m. |
| One inch | | = 2.54 cm. |

TABLE FOR THE CONVERSION OF GRAMS INTO GRAINS, CENTIMETERS INTO INCHES, AND LITERS INTO QUARTS.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Grams into Grains. | 15.4328 | 80.5647 | 46.2970 | 61.7294 | 77.1617 | 92.5941 | 108.0265 | 123.4588 | 138.8911 |
| Centimeters into Inches. | 0.3937079 | 0.7874158 | 1.1811237 | 1.5748316 | 1.9685395 | 2.3622474 | 2.7559553 | 3.1496632 | 3.5433711 |
| Liters into Imp. Quarts. | 0.839066 | 1.76132 | 2.64198 | 3.52264 | 4.40330 | 5.28396 | 6.16462 | 7.04528 | 7.92594 |
| Liters into U. S. Quarts. | 1.05708 | 2.11415 | 3.17123 | 4.22830 | 5.28538 | 6.34245 | 7.39953 | 8.45660 | 9.51368 |



30. TABLE

FOR THE CONVERSION OF DEGREES ON THE CENTIGRADE THERMOMETER
INTO DEGREES OF FAHRENHEIT'S SCALE.

$$C.^{\circ} = (F.^{\circ} - 32) \frac{5}{9}; \text{ and } F.^{\circ} = \frac{9}{5} C.^{\circ} + 32.$$

| CENT. | FAHR. | CENT. | FAHR. | CENT. | FAHR. |
|-------|-------|-------|-------|-------|-------|
| 0 | 0 | 0 | 0 | 0 | 0 |
| -50 | -58.0 | 17 | 62.6 | 60 | 140.0 |
| -45 | -49.0 | 18 | 64.4 | 61 | 141.8 |
| -40 | -40.0 | 19 | 66.2 | 62 | 143.6 |
| -35 | -31.0 | 20 | 68.0 | 63 | 145.4 |
| -30 | -22.0 | 21 | 69.8 | 64 | 147.2 |
| -25 | -13.0 | 22 | 71.6 | 65 | 149.0 |
| -20 | -4.0 | 23 | 73.4 | 66 | 150.8 |
| -19 | -2.2 | 24 | 75.2 | 67 | 152.6 |
| -18 | -0.4 | 25 | 77.0 | 68 | 154.4 |
| -17 | + 1.4 | 26 | 78.8 | 69 | 156.2 |
| -16 | 3.2 | 27 | 80.6 | 70 | 158.0 |
| -15 | 5.0 | 28 | 82.4 | 71 | 159.8 |
| -14 | 6.8 | 29 | 84.2 | 72 | 161.6 |
| -13 | 8.6 | 30 | 86.0 | 73 | 163.4 |
| -12 | 10.4 | 31 | 87.8 | 74 | 165.2 |
| -11 | 12.2 | 32 | 89.6 | 75 | 167.0 |
| -10 | 14.0 | 33 | 91.4 | 76 | 168.8 |
| -9 | 15.8 | 34 | 93.2 | 77 | 170.6 |
| -8 | 17.6 | 35 | 95.0 | 78 | 172.4 |
| -7 | 19.4 | 36 | 96.8 | 79 | 174.2 |
| -6 | 21.2 | 37 | 98.6 | 80 | 176.0 |
| -5 | 23.0 | 38 | 100.4 | 81 | 177.8 |
| -4 | 24.8 | 39 | 102.2 | 82 | 179.6 |
| -3 | 26.6 | 40 | 104.0 | 83 | 181.4 |
| -2 | 28.4 | 41 | 105.8 | 84 | 183.2 |
| -1 | 30.2 | 42 | 107.6 | 85 | 185.0 |
| 0 | 32.0 | 43 | 109.4 | 86 | 186.8 |
| + 1 | 33.8 | 44 | 111.2 | 87 | 188.6 |
| 2 | 35.6 | 45 | 113.0 | 88 | 190.4 |
| 3 | 37.4 | 46 | 114.8 | 89 | 192.2 |
| 4 | 39.2 | 47 | 116.6 | 90 | 194.0 |
| 5 | 41.0 | 48 | 118.4 | 91 | 195.8 |
| 6 | 42.8 | 49 | 120.2 | 92 | 197.6 |
| 7 | 44.6 | 50 | 122.0 | 93 | 199.4 |
| 8 | 46.4 | 51 | 123.8 | 94 | 201.2 |
| 9 | 48.2 | 52 | 125.6 | 95 | 203.0 |
| 10 | 50.0 | 53 | 127.4 | 96 | 204.8 |
| 11 | 51.8 | 54 | 129.2 | 97 | 206.6 |
| 12 | 53.6 | 55 | 131.0 | 98 | 208.4 |
| 13 | 55.4 | 56 | 132.8 | 99 | 210.2 |
| 14 | 57.2 | 57 | 134.6 | 100 | 212.0 |
| 15 | 59.0 | 58 | 136.4 | | |
| 16 | 60.8 | 59 | 138.2 | | |

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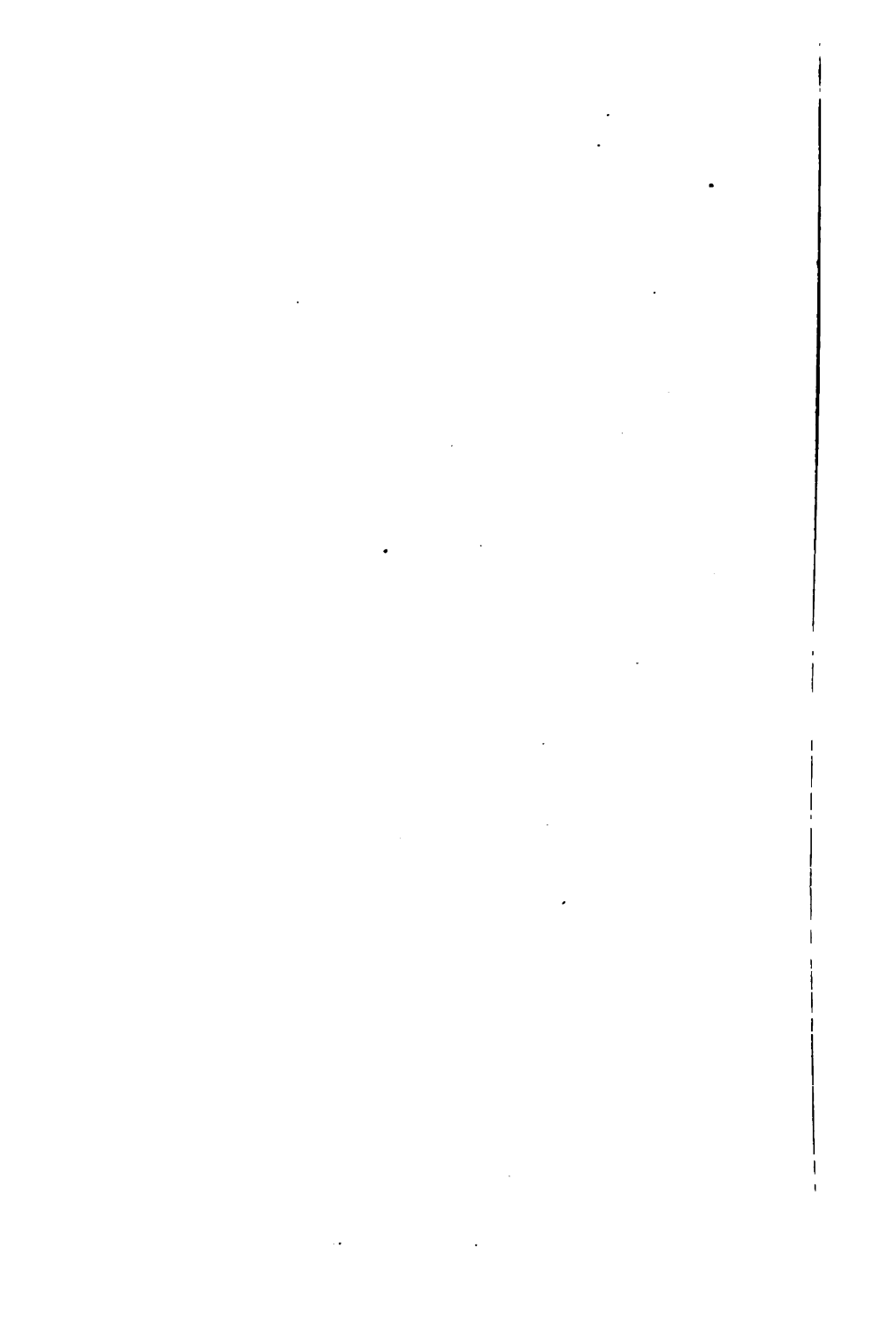
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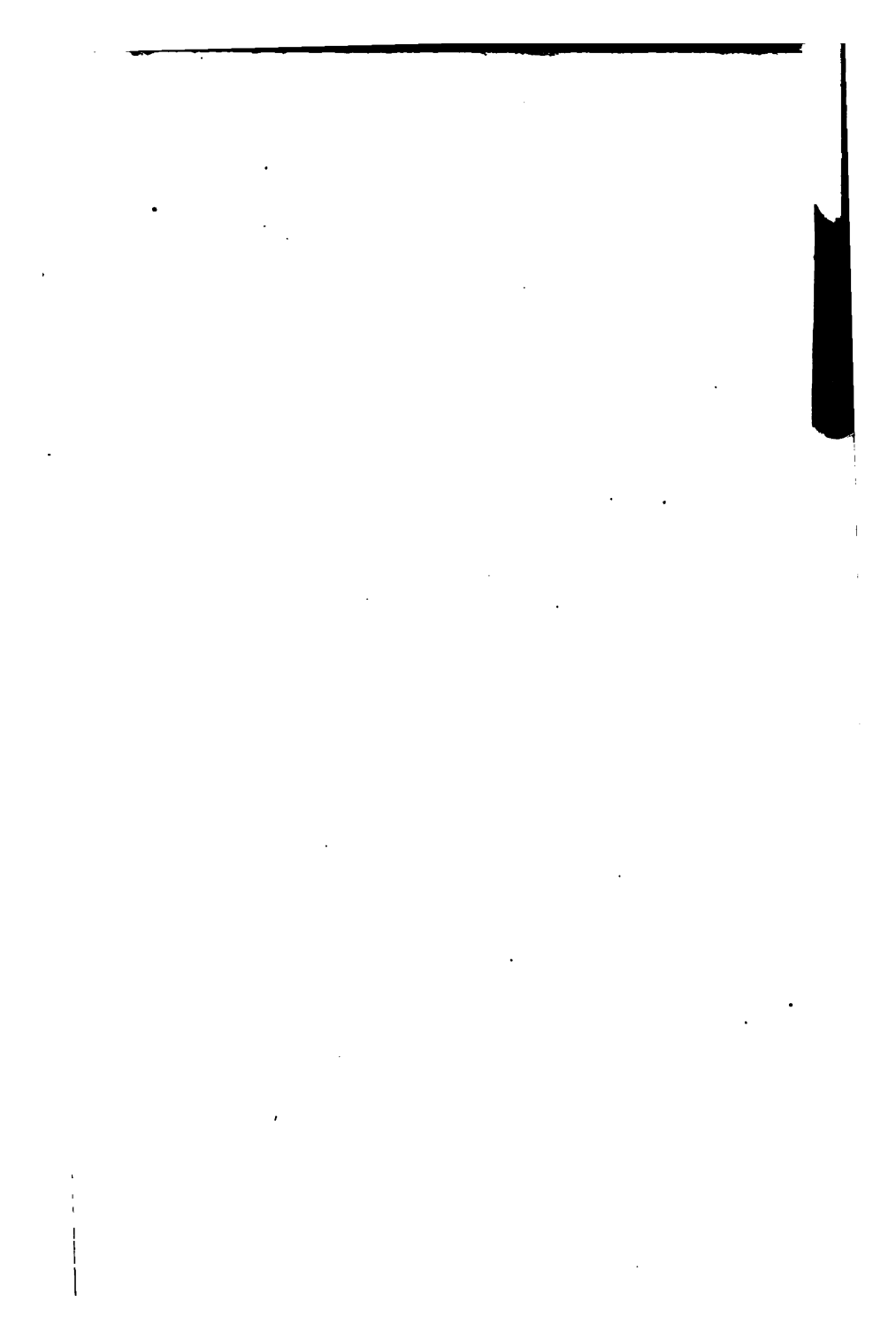
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